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**Thesis Title:**

***Driving Forces Behind Mergers and Acquisitions Activity:  
The Aggregate Economic Activity and the Stock Market***

By

Leonidas V. Tzonis

A thesis submitted in partial fulfilment of the requirements of the  
University of Northumbria at Newcastle for the degree of Doctor of  
Philosophy

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## **Abstract**

### **Driving Forces Behind Mergers and Acquisitions Activity: The Aggregate Economic Activity and the Stock Market**

By Leonidas V. Tzonis

The present thesis, motivated by controversies in the literature investigates a series of empirical issues relating to mergers and acquisitions activity in the UK. More specifically, it seeks answers to the following questions: do mergers come in waves, and is there a significant relationship between the aggregate mergers and acquisitions activity, the business cycle and the stock market, both at aggregate and industrial level? Are the stock market mis-valuation and the market timing ability of manager among the driving forces behind merger waves? The focal point is the UK corporate control market over the last twenty years (1985-2005).

The main results emerging from the empirical analysis indicate that there exist three distinctly different types of behaviour (regimes) in the series of mergers and acquisitions numbers, both at aggregate and industrial level. Moreover, the contemporaneous relationship between the mergers and acquisitions activity in the UK with the Stock Market and the aggregate economic activity (Business Cycle), is found to be significant, at aggregate level. Finally, consistent evidence which suggests that stock market mis-valuation and the market timing ability of manager is more likely to drive the corporate control market is provided.

*Dedicated to Vicky,  
for the love, the support, the patience.  
for what she is, for what we have.*



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The material contained in this thesis has not been previously submitted for a degree in this or any University.

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## **Chapter 1: Introduction**

### ***1.1 Introduction***

The market for corporate control operates continually as companies grow and evolve. It appears to move in a cyclical manner with different levels of mergers and acquisitions<sup>1</sup> activity. In 1890 Alfred Marshall suggests that “the subject is one on which it would be rash to speak confidently. We of this generation, being hurried alone in a world of change, cannot measure accurately the forces at work and it is probable that the best guesses we can make will move the smiles of future generations”<sup>2</sup>. His remark still seems appropriate more than a century after he made it.

Over the past century, the literature recorded significant upsurges in the numbers of takeovers in the UK<sup>3</sup> in the 1920s and 1950s; and in the early 1960s, late 1960s to early 1970s, late 1980s, and late 1990s. With respect to their relative importance Hughes and Singh (1980) report that in the period 1948 to 1958 UK mergers accounted for more than two thirds of corporate deaths and in the period 1959 to 1972 for four fifths. In the decade 1972 to 1982 one in three of the largest 730 quoted companies were acquired, whilst in the mid-1980s 137 of the largest 1000 non financial were taken over in just four years (1982 to 1986). In terms of the size

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<sup>1</sup> The terms ‘merger’, ‘acquisition’ and ‘takeover’ are used interchangeably throughout this thesis.

<sup>2</sup> Alfred Marsall, *Some Aspects of Competition*, reprinted in R.L. Smyth (ed.), *Essays in the Economics of Socialism and Capitalism*, 1964, p. 101; reproduced from Hannah (1974).

<sup>3</sup> For similar US statistics see Steiner (1975), Mueller (1986) and Dodd (1986).

of these transactions, the total expenditure on acquisitions appears to be rising; in 1995 it reached an all time record of over £32.6bn, followed by similar levels in subsequent years.

These figures leave no room for doubt that an extremely active market for corporate control<sup>4</sup> exists. The sheer size of this market makes it a considerable means through which to canvass existing economic theory. In fact, its suggested efficiency characteristics are used to form an important line for defence of the neoclassical theory of the firm and its central assumption of profit maximisation, through the concept of 'economic natural selection' (Alchian, 1950; Friedman, 1953; Johnson, 1968).

Therefore, a significant body of existing literature examines the efficiency indicators of the merger process. However, profitability based studies seem to question the efficiency enhancing character of takeovers by finding a negative effect on the profitability of the acquirer (e.g. Meeks, 1977; Cosh, Hughes and Singh, 1980; Cowling et. al, 1980; Ravenscraft and Scherer, 1987; Hughes, 1987; Berkovtch and Narayannan, 1993; Chatterjee and Meeks, 1996). On the other hand, research using event study methodology finds positive abnormal returns around the bid period (e.g. Firth, 1980; Jensen and Ruback, 1983; Franks and Harris, 1986). More recently, however, longer run event studies have shown consistently negative returns to acquirers, questioning not only the efficiency of the process but also the

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<sup>4</sup> The term is due to Manne (1965) and refers to the market for ownership of corporations via acquisitions.

efficiency of the stock market and the validity of the residual analysis methodology<sup>5</sup> (e.g. Limmack, 1991, 1997; Agrawal et. al, 1992; Higson and Elliot, 1994; Gregory, 1997). Another major strand of research examines the impact of mergers on market structure and economic welfare and concentration as an alternative way of assessing the efficiency character of the process (e.g. Utton, 1971; Hannah and Kay, 1977; Hughes and Singh, 1980; Hughes and Kumar, 1985; Hughes, 1993).

Although important for merger policy, these lines of research have been particularly insightful in discriminating between the plethora of proposed motives for takeovers, and towards identifying the driving forces behind the merger waves.

Fundamental to the research for such micro explanations has been the attempt to identify factors that discriminate between acquirers and their targets with respect to their respective economic and financial characteristics. Research has shown that usually the main discrimination is size, while targets do not seem to generally under-perform as 'efficiency theories' would suggest (e.g. Singh, 1971, 1975; Meeks, 1977; Cosh, Hughes and Singh, 1980; Levine and Aaravitch, 1981; Kumar, 1984; Palepu, 1986; Powell and Thomas, 1994; Powell, 1997). Furthermore, the two studies by Singh provide early evidence that the already great degree of overlap of characteristics between acquirers and their targets becomes greater during a period of rising merger activity. Despite its importance this aspect

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<sup>5</sup> See also Dimson and Marsh (1986) for a criticism on event studies and specifically where CAPM methodologies are used. For simple explanation of the implication of negative long-run returns on the underlying Efficient Market Hypothesis, see Chatterjee and Meeks (1996).

of the merger process has been researched further, relatively recently. The empirical evidence suggests that discriminating factors vary in strength and nature depending on whether the period under investigation could be characterised as a period of 'rising' or 'falling' merger and acquisition activity (e.g. Cosh, Hughes, Lee and Singh, 1990; Higson and Elliot, 1993; Antoniou, Owen and Pescetto, 1998).

This highlights a weakness of the micro-framework. More specifically, highlights its inability to explain or incorporate the recorded upsurge in merger activity during specific periods. Apparently, the micro-based theories cannot explain, by themselves, why the process should be episodic. Antoniou et al. (1998) argue that "particularly puzzling is the observation that even with obvious changes to its market or financial posture, a firm could become a target for acquisition at one particular point in its life but not at others"<sup>6</sup>. Generally, a characteristic of all the micro-studies has been the lack of strong statistical results and explanatory power in discriminating between competing theories and financial characteristics of companies involved in takeovers.

This empirical failure of micro-studies, along with the fact that casual observation of aggregate mergers and acquisitions activity shows it to be cyclical and generally to follow the business cycle (pro-cyclical), motivated another line of research towards a more encompassing theory of merger activity. Weston, Chung and Hoang (1990) describe the need for such a direction of research: "[a] complete

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<sup>6</sup> Antoniou, Owen and Pescetto (1998), p.2



theory of mergers should have implications on the timing of merger activity. As the matter stands, there does not exist an accepted theory which simultaneously explains motivations behind mergers, characteristics of acquiring and acquired firms, and the determinants of the levels of aggregate merger activity”.<sup>7</sup>

Brealey and Mayers (1991) consider wave behavior of mergers and acquisitions as being among the ten most important unsolved issues in financial economics. Various researchers attempted to shed light in this direction. The existing literature can broadly be divided into two categories. Firstly there are papers using time series methodologies found in general that acquisition activity is random and therefore unpredictable. Shugart and Tollison (1984) found that numbers of acquisitions are best described by a random walk and declared that this meant that the series was random. Furthermore Chowdhury (1993) used unit root tests to show that the changes in mergers number are random although he did not investigate levels of mergers activity. However, Golbe and White (1993) observed that Shugart and Tollison (1984) appear to have confused the analysis of acquisitions level with that of differences and their final conclusion actually implies that, whilst differences are random, takeovers levels are autoregressive.

The second group of literature concentrated on the influence that macroeconomic factors have on takeover activity levels. In one of the very first papers in the area Gort (1969) found concrete links between the economic conditions and the level of acquisitions activity. More specifically, he proposed that acquisitions take place

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<sup>7</sup> Weston, Chung and Hoang (1990), p.276

because the economic conditions change in such a way that the values of the firm were significantly altered. Following Gort (1969), Steiner (1975) attempted to link the level of activity in the corporate control market to specific macroeconomic factors, such as stock prices and GNP. At a later stage Melicher, Ledolter and D'Antonio (1983) proposed their “merger activity – economic prosperity” theory which links changes in the expected level of economic growth and the capital market conditions to acquisition levels. On the other hand Golbe and White (1988) used regression models to analyze the link between the level of takeovers in States and the economic situation. According to their findings similar economic variables seems to be significant.

More recently Town (1992) investigated the behaviour of mergers and acquisitions in the UK , making use of the Markov switching model with no autoregressive dynamics and constant transition probabilities as Hamilton (1990) proposed and applied by Engel and Hamilton (1990) in the context of exchange rates. These models have the capacity to capture abrupt changes in the evolution of a given time series. According to his empirical findings M&A appeared to display analogous behaviour to the ‘long swings’ in the exchange rate literature. However the incidence of M&A waves is not exactly the same, although there are some similarities. Moreover the random walk specification is strongly rejected.

Overall, existing literature finds a weak and uncertain relationship between merger activity and macroeconomic variables, while the most pronounced relationship

seems to be with financial variables and specifically with share price level. Attempts to formulate a complete theory based on these results has proved to be very difficult and so such attempt, as yet, commands general or even partial acceptance. This has led to the common belief that if merger activity has indeed underlying economic motives, these must be “here today and gone tomorrow”<sup>8</sup>. This observation possibly expresses a deeper belief that there is no formal relationship between merger activity and the underlying economic environment. A belief that probably stems from the inability to pinpoint the changes in this environment (real and / or financial) that causes and supports mergers and acquisitions. However, this is at odds with both the general (pro-cyclical) pattern of the process and the fact that evidence from the micro-literature suggests the possible presence of macro- rather than micro-determinants<sup>9</sup>.

The apparent puzzle may be due to a couple of related factors. The first one is the lack of understanding of the dynamic behaviour of the process, and the second, the quality of existing results, both of which seem related to the lack of an unbiased long series of aggregate merger activity. One manifestation of this problem is the evidence from relatively recent univariate merger studies that suggests the failure of linear models in adequately describing the process (Town, 1992; Linn and Zhu, 1997; Resende, 1999). If true, this would imply that results from the merger / macro research are subject to the spurious correlation problem (Yule, 1926).

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<sup>8</sup> Brealey and Mayers (1991), p.846

<sup>9</sup> One notable attempt to identify these empirically at the micro / macro level is Antoniou, Owen and Pescetto (1998). Similarly, other conceptually interesting attempts surround the ‘merger as investment’ approach (Mueller, 1969; Holly and Longbottom, 1988; Bittlingmayer, 1996).

More recently, Shleifer and Vishny (2003) and Rhodes-Kropf and Viswanathan (2004) proposed theories of takeovers (*Market timing theory*) related to the neoclassical theory. In this theory, transactions are driven by *stock market valuations* of the merging firms. The fundamental assumption of these models is that financial markets are inefficient, so some firms are valued incorrectly. Most importantly, however, the controversial evidence in the area highlights the need to fully understand the nature of the process before the attempt to explain it.

## ***1.2 Aims and Objectives of the Thesis***

This study attempts to improve the understanding of the nature of the aggregate mergers and acquisitions activity and its components. In doing so, it aims to provide an analytical framework in order to identify the elusive determinants of merger activity, where the present results suggest that these may be found at aggregate level.

More specifically, this thesis has the following main objectives in studying further the characteristics of the aggregate mergers in the UK. First, it aims to determine formally the presence of mergers waves both at aggregate and industrial level. It attempts to extend existing research by allowing the series to follow three regimes with different mean values enabling the series to be modeled using multiple time series representations. The three regimes defined here represent the series (1) in

decreasing mergers activity periods at the end of a merger wave, (2) in normal mergers activity period, and (3) in rising mergers activity period at the beginning of a merger wave. Examining each of these different types of behavior provides a considerably more informative picture of the behavior of the series over time than has been previously available.

Second, it attempts to examine the relationship the Mergers and Acquisitions activity in the UK with the Stock Market and the aggregate economic activity (Business Cycle), both at aggregate and industrial level. Moreover, it is reasonable to consider that the relationship between the Mergers and Acquisitions activity, the Stock Market and the Business cycle might be significantly different during periods of falling, rising or stable Mergers activity.

Finally, it attempts to empirically test the Shleifer and Vishny's (2003) theoretical propositions that stock market mis-valuations drive mergers waves. Specifically, the main objective is to test the undervaluation side of the story within a market / manager rationality framework.

This thesis attempts to contribute towards a deeper understanding of the economic factors underlying Mergers and acquisitions activity

## ***1.2 Structure of the Thesis***

The remaining of this thesis is structured as follows:

Chapter two provides an overview of mergers and acquisitions. It is not designed to include a detailed literature review of the area, but an overall picture of the main terms and characteristics of corporate takeovers.

Chapter three is designed to analyze the behavior of the corporate control market in the UK during a period that incorporates excessive acquisitions activity in this country. More specifically, chapter three has three main objectives in studying further the characteristics of the aggregate mergers in the UK. First, it aims to determine formally the presence of mergers waves making use of the Markov switching models with no autoregressive dynamics and constant transition probabilities along the lines of Hamilton (1990) and applied by Engel and Hamilton (1990) in the context of exchange rates. These models have the capacity to capture abrupt changes in the evolution of a given time series. It extends existing research by using a Markov Switching Model, allowing the series to follow three regimes with different mean values enabling the series to be modeled using multiple time series representations. The three regimes defined here represent the series (1) in decreasing mergers activity periods at the end of a merger wave, (2) in normal mergers activity period, and (3) in rising mergers activity period at the beginning of a merger wave. Examining each of these different types of behavior

provides a considerably more informative picture of the behavior of the series over time than has been previously available. The dataset employed covers mergers activity in the UK from 1969:1 through 2003:4. Second, it attempts to examine the relationship the Mergers and Acquisitions activity in the UK with the Stock Market and the aggregate economic activity (Business Cycle). Finally, it is reasonable to consider that the relationship between the Mergers and Acquisitions activity, the Stock Market and the Business cycle might be significantly different during periods of falling, rising or stable Mergers activity.

Chapter four attempts to investigate the behavior of mergers and acquisitions, at sectoral (industrial) level, making use of the Markov switching models with no autoregressive dynamics and constant transition probabilities along the lines of the third chapter. The focus of the chapter is on the UK case, for which the longest consistent available data series on sectoral level are considered. Quarterly disaggregated data by sector of the acquiring firm is used; specifically we consider the number of mergers and acquisitions of independent companies by industrial and commercial companies. Sector classification changes limited our sample to the period 1986:1 to 2005:2, dis-considering in addition sectors where mergers and acquisitions were virtually nonexistent, such as the tobacco industry. The basic source is the Thomson One Banker Database. Sectoral data for the stock market (FTSE Sector Indexes) were downloaded from Datastream. Moreover, chapter four attempts to examine the relationship between the sectoral mergers and acquisitions activity in the UK with the stock market and the aggregate economic

activity (Business Cycle) at a sectoral level. Finally, it considers whether or not the relationship between the mergers and acquisitions activity (in each one of the sectors), the stock market and the Business Cycle might be significantly different during periods of falling, rising or stable mergers activity (within the sector).

Chapter five's main purpose is to test empirically, the hypothesis developed by Shleifer and Vishny (2003) by employing UK data for the period 1986 to 2006. Shleifer and Vishny (2003) propose a theory of acquisitions related to the neoclassical theory, but also able to accommodate the additional evidence. In their theory, mergers are driven by stock market valuations of the merging firms (stock market driven acquisitions). The fundamental assumption of the model is that financial markets are inefficient, so some firms are valued incorrectly. In contrast, managers are completely rational, understand stock market inefficiencies, and take advantage of them, in part through mergers and acquisitions decisions. Mergers in this model are a form of arbitrage by rational managers. For the purpose of this, the Brown and Warner's (1985) standard event study methodology is adopted.

Finally, Chapter six summarizes and suggests some directions for further research for the elusive determinants of aggregate merger and acquisition activity based on the results, methods and data from this study towards a complete theory of merger and acquisition activity.



## **Chapter 2: Overview of Mergers and Acquisitions**

### ***2.1 Introduction***

Why would one firm want to acquire or merge with another? Are there really no other less painful ways for a firm to grow? Does the management of one firm really have nothing better than to try to obtain another firm's management's pie – the whole of it? Who and what would be the driving force behind such activity? What are their reasons? Do these reasons outweigh the obstacles? How would they do it? Who are the post-merger/acquisition winners and losers – is it even possible to quantify the gains and the losses? It will be attempted to answer the above questions on this key area of corporate finance over the next few pages. A try to make sense of the empirical data to back up or, perhaps, question some of the arguments before addressing the phenomenon of merger waves which sweep like tsunamis through the corporate world seemingly at random every decade or so, leaving behind it a somewhat altered landscape, will be made.

### ***2.2 Motives of Mergers and Acquisitions***

It would be sensible to talk about synergy here, i.e. that the whole is “worth” more than the combination of its parts or, in an example of two firms A and B merging into one firm AB,  $PV(AB) > PV(A) + PV(B)$ . It is not unreasonable to say that firm

A should go ahead and acquire firm B if the cost of this acquisition is less than the gain associated with it.

All that is pretty straightforward but before going on it is important to discuss which specifics of an acquisition could give those “gains”. Acquisitions are classified as below:

1. Horizontal Acquisition – the acquired firm comes from the same industry as the acquiring firm. They are competitors in their product market. A BP-Amoco deal would be an example.
2. Vertical Acquisition – the acquired firm comes from a different step in the production process, e.g. the AT&T-TCI arrangement. The idea is to get closer to the raw materials or to the eventual consumer.
3. Conglomerate Acquisition – the acquired firm is unrelated to the acquiring firm – once fashionable in the 1960s and 1970s in the midst of belief in the universal nature of “good management”, but were broken up in the 1980s. Hanson is an example.

So, bearing in mind the above classifications, it can be examined where the potential gains could come from, also obtaining some understanding of the motives:

### ***2.2.1 Cost Reduction***

Assuming that the rule of economies of scale holds true it is expected that a merger would bring a reduction in the average cost of production and the overhead costs.

Economies of vertical integration makes the co-ordination and administration of closely related operating activities easier but more vertical integration is not necessarily better. For example in the automobile industry where in contrast to the all-in-house set ups of the General Motors from the 1950s and 1960s, in 1990s, it was found by Ford that it was actually cheaper to buy parts from outside suppliers.

One firm could acquire another to make better use of existing resources or to provide missing ingredients for success. A small firm could have a unique product and the large firm could have the engineering and other resources to “make it happen” for the smaller firm.

A merger can be looked at for the purpose of eliminating the inefficient management, where new management can, for example, start serving the shareholders as opposed to concentrating on the management interests.

### ***2.2.2 Revenue Enhancement***

It is claimed that greater operating revenues from improved marketing can be produced. Previously ineffective advertising efforts, weak existing distribution network and unbalanced product mix can all be improved.

Strategic benefits, i.e. opportunities to take advantage of the competitive environment in certain situations may materialize. Perhaps, the firm can enter a new market – both geographically and from a business or product perspective. For example, Procter and Gamble's acquisition of the Charmin Paper Company.

Smaller companies in a market could look towards building up a critical mass to muscle in on the bigger players. Mature company with spare cash, which is finding it hard to grow organically can invest in a younger company and thus fulfil its growth ambitions.

One firm could buy another to reduce competition and enjoy monopoly profits, which could, of course, attract the attention of the relevant anti-monopoly agencies (e.g. MMC in the UK, FTC in the USA).

The acquiring target may be undervalued. This point relies on the argument that the markets are inefficient in the valuation of the target firm.

### ***2.2.3 Tax Gains***

Sometimes firms have tax losses they cannot take advantage of and they need taxable profits to take advantage of these. A merger can sometimes accomplish this; however, one has to bear in mind that laws may prevent an acquisition if its sole purpose is to avoid taxes.

If a firm has spare cash, it can use it to purchase another firm's shares as opposed to increase dividends to the shareholders. This way the taxes on the extra dividends are avoided. Also, the firm pays little corporate tax on dividends received from the shares of the acquired firm as 70% of the dividend income received from the acquired firm is excluded from the corporate income tax.

#### ***2.2.4 Dubious Reasons***

Diversification, where there is the obvious reduction in risk, but diversification is easier and cheaper for the stockholder than for the corporation. No one has shown that investors pay a premium for diversified firms; in fact, discounts are common. The example with the Kaiser Industries pre-break-up share price shows that diversification does not increase value.

Increasing earnings per share is often a deceptive game. This can occur in a situation, where, say Firms A and B have equal earnings per share levels at the start of play, yet B has the share value that is only one half of A's share value due to the fact that its growth prospects are lower and thus the price-earning ratio is lower too. If, say, the merger produces no economic benefits, via the 1-for-2 share exchange in a merger (1 share of A for every 2 shares of B), it is easy to see that the earnings-per-share level of the combined firm will go up, given the value of the new firm's shares are the same as A's. Some financial manipulators will try to play

on this fact to trumpet about how well the firm is doing post-merger (even though economically overall nothing has changes) in an attempt to fool the market. One might play this game more than once but eventually the trumped up pyramid will collapse as the expansion via merger in this way cannot continue infinitely and one day the earnings growth will cease and the charade will collapse.

When two firms merge, combined firm can borrow at lower interest rates than either firm could do separately as, effectively, they now guarantee each other's debt, which makes the debt less risky with lenders thus demanding lower interest rates; however, the two firms' shareholders are the losers now as they lose by having to guarantee each other's debt. (Watson & Head, 1998; Ross et al, 2005)

So, as has been shown, there is quite an array of reasons for acquiring another firm, so it is now time to examine how these plans are put into practice.

### ***2.3 How? – Ways of putting those plans into life***

The main ways of acquiring another firm and their relative pros and cons will now be considered.

#### ***2.3.1 Merger (or Consolidation)***

Merger is absorption of one firm by another. The acquiring firm keeps its name and identity and obtains all of the assets and liabilities of the acquired firm. After the merger, the acquired firm ceases to exist. Consolidation is the same as a merger but a brand new firm is created. Both firms involved terminate their previous legal existence and become part of the new firm.

A merger is legally straightforward, cheaper than other types of acquisition and does not involve the title transfer of the acquired asset to the acquiring firm; however, it has to be approved by a certain percentage (usually at least 2/3) of the stockholders of each firm. In addition, the appraisal rights of the shareholders of the target firm can lead to difficulties with the dissenting shareholders. (Ross et al, 2005)

### ***2.3.2 Acquisition of Stock***

In this scenario the buyer will simply acquire the target's stock in exchange for cash, shares or other securities. Shareholders can be dealt with on individual basis. The target's management can be bypassed – of course, the buyer would want them to cooperate but if that is proving difficult to achieve, the buyer can simply try to obtain an effective majority of outstanding shares with the subsequent removal of the difficult management. As one can understand an acquisition of stock is often unfriendly. The shareholders are in a position to reject the tender offer (public offer to buy the shares). If a minority of shareholders are holding out, a formal merger might be required to complete the proceedings.

There are the issues with financing the acquisition of stock with cash or with shares. On the one hand acquisitions for cash often have to be financed by debt – either borrowing from banks or by issuing debt securities. Of course, the buyer has to keep an eye on its gearing and it is not rare to sell off parts of the acquired firm to bring this gearing down. On the other hand, cash acquisitions are often cheaper as the share-funded acquisition often have to be overly generous to the target firm's shareholders to overcompensate for any potential future fall in price of the said shares and can lead to a situation where the more the predator firm pushes for the target to accept the share offer, the more suspicious the target firm becomes, the harder the bargain it drives. Then again, the share offer does give the shareholders



of the target firm the chance to share in potential future good performance of the predator firm. The acquisition of stock is more expensive to a buyer than the merger due to its unfriendly nature.

Mixed bids - a mixture of stock and cash alternative – are becoming more common in the UK. Mixed bids are perceived as being more acceptable to the target company's shareholders as they can select the method of payment that best suits their preferences and tax positions (we will discuss tax considerations shortly). On the other hand, the target company's shareholder could rush to dump their shares if, for example, the offer is such that initially cash is paid for the shares and after a certain time or financial limit, only shares will be used for the exchange (two-tier offer). (Watson & Head, 1998; Ross et al., 2005)

Finally, tax considerations should be taken into account. In a taxable acquisition, the selling shareholders are treated as having sold their shares and thus must pay a capital gains tax. In this case, the assets of the selling firm are also re-valued, the resulting write-up or write-down is treated as taxable gain or loss and tax depreciation is recalculated on the basis of the restated asset values. In tax-free acquisition, the selling shareholders are seen as exchanging their shares for similar new ones and thus no capital gains or losses are recognised. Proper tax planning maximises the value of the acquisition transaction for both buyers and sellers (Abahoonie & Brenner, 1994).

The use of securities other than the ordinary shares of the predator is now rare. The use of straight debenture and loan stock does not really have the confidence of the seller. Convertible bonds – which give the possibility of buying into the predator company's future wealth – are slightly more attractive. Finally, preference shares are not a very desirable tool from the predator's point of view due to their lower flexibility. The popularity of the use of debt security packages was killed off by the high inflation in the 1970s, caused by the oil crises. (Watson & Head, 1998).

Therefore, in mergers and tender offers, the acquiring firm buys the voting common stock of the acquired firm.

### ***2.3.3 Other forms of takeover***

1. Proxy contests – occur when a group of shareholders attempt to gain controlling seats on the board of directors by voting in new directors. A proxy authorises the proxy holder to vote on all matters in shareholders' meetings. Proxies from the rest of the shareholders are solicited by insurgent shareholders.

2. Going private transactions – all the equity shares of a public company are purchased by a small group of investors – usually some of the current management and outside investors. The shares are de-listed and are thus taken off the open market.

3. Acquisition of Assets - One firm can acquire another by buying all of its assets. The selling firm's shareholders need to vote in this situation, this avoids the problem of having minority shareholders. The legal process is expensive.

## ***2.4 Mergers and Acquisitions Defences***

There are several methods of resistance available to the target firm – before and after a bid has been launched.

### ***2.4.1 Pre-Bid Defences***

1. Improving operational efficiency – making production more rational, cutting overheads and improving labour productivity can raise the firm's EPS and share price.
2. Examining asset portfolios and making necessary divestments – sell off non-core and underperforming businesses and concentrate on the growth markets. This will again raise EPS and share price as well as leading to higher profits.
3. Restructuring of equity – for example, share repurchase to make it more difficult for predators to get a foothold or increased gearing to make the firm a less attractive target.
4. Management retrenchment packages – also known as golden parachutes, these are extremely generous termination packages for senior management.

5. Ensuring good investor relations – good relations with investors and analysts and keeping them “sweet” making the acquisition more difficult and expensive.
6. Strategic defence via cross-holding – equity in “friendly” hands means fewer headaches about potential attacks.
7. “Poison put” – existing bondholders can demand repayment if there is change in company control as the result of hostile takeover.
8. Amendments to the company charter – such shark-repellent amendments such as staggered board, supermajority, fair price, restricted voting rights and waiting period conditions.

#### ***2.4.2 Post-Bid Defences***

1. Rejection of the initial offer – indication that the target firm “will fight”.
2. Pre-emptive circulation of shareholdings – explain why the bid is not in their interest.
3. Formulation of a defence document protecting the target and criticising the predator and its offer.
4. Profit announcements and forecasts to show the market that the firm is actually doing better than the market values it.
5. Dividend increase announcement – “sweetening up” the shareholders.
6. Revaluation of assets – to make the company look stronger and more valuable.

7. White knight – someone who will take over in a friendly manner, not turning the place on its head; however, any information passed on to the white knight must also be passed on to the others in the bidding process.
  8. Pacman defence – launch a bid for the predator! Expensive to carry out but was successfully used by Cities Service against Mesa in the 1980s.
  9. Acquisitions and divestments – buy businesses incompatible with the predator's interests or sell off what potential predators might have been interested in.
  10. Litigation – file suit against bidder for violating antitrust or security laws.
- (Watson & Head, 1998; Ross et al, 2005)

As has been seen, there are many ways open for the target firm raise the stakes and the cost of the game to the predator. Interesting situations arise when the shareholders and the management come into conflict over the decisions. In the case when AlliedSignal went for AMP in 1998, where, despite majority of the shareholders agreeing to the tender offer, a poison pill caused a time delay, during which time the management went to the state legislature. The case dragged on until a white knight was found, which paid more for the shares than AlliedSignal was offering. In the end the management proved that it was acting in the shareholders' interest and the poison pill dragged out the negotiations making the AlliedSignal offence too slow and expensive.

## ***2.5 Empirical Evidence on Mergers and Acquisitions Gains***

From the above, one can see that generally the winners seem to be the predator's management and the target's shareholders. The losers are, firstly, the target firm's management and other employees, who tend to get laid off while merger savings are obtained and the predator's shareholders. The bondholders would probably do well (at the expense of the shareholders) as the default risk is lowered. Examining somewhat contradictory empirical evidence, which depends on the source, period and sector the results as below were found.

One method to quantify the benefit of mergers and acquisitions is to study the pre- and post-bid announcement share prices. The focus is on abnormal returns – the difference between the actual stock returns and a market index or a control group of stocks. Studies found that the target firm's shareholders do experience significant positive abnormal returns, whilst the predator firm's shareholder's returns fluctuate close to zero. In comparison, in periods well before the acquisition, the predator companies were the ones with the abnormal positive returns, with the targets sporting negative ones. Ross et al (2005) summarise the information from the Jensen and Ruback (1983) findings for the abnormal stock price changes associated with successful and unsuccessful corporate takeover bids in the short run:

SUCCESSFUL			UNSUCCESSFUL		
Takeover method	Target	Bidders	Takeover method	Target	Bidders
Tender offer	30%	4%	Tender offer	-3%	-1%
Merger	20%	0%	Merger	-3%	-5%
Proxy Contest	8%	n.a.	Proxy Contest	8%	n.a.

The return to the shareholders of targets of unsuccessful merger/tender offer, measured from the offer date to the cancellation date, is negative; however, this does not take account of the event that a future takeover offer could be where additional gains could be realised.

For the long-term results, Ross et al (2005) turn to Loughran and Vijh (1997), who give the following data on abnormal 5-year stock returns of acquiring firms from 1970 to 1989:

Acquirers using unfriendly cash tender offers	61.7%
Acquirers who pay cash (both friendly and unfriendly)	18.5%
All acquirers	-6.5%
Acquirers using stock	-24.2%

The above points to the following conclusions:

1. In the long run, the shareholders of the acquiring companies experience below average returns.

2. Cash-financed mergers are different than stock-financed ones.
3. Friendly and unfriendly cash acquirers perform differently, suggesting that unfriendly acquirers may be keener on removal of poor management and improving the performance in the long run.

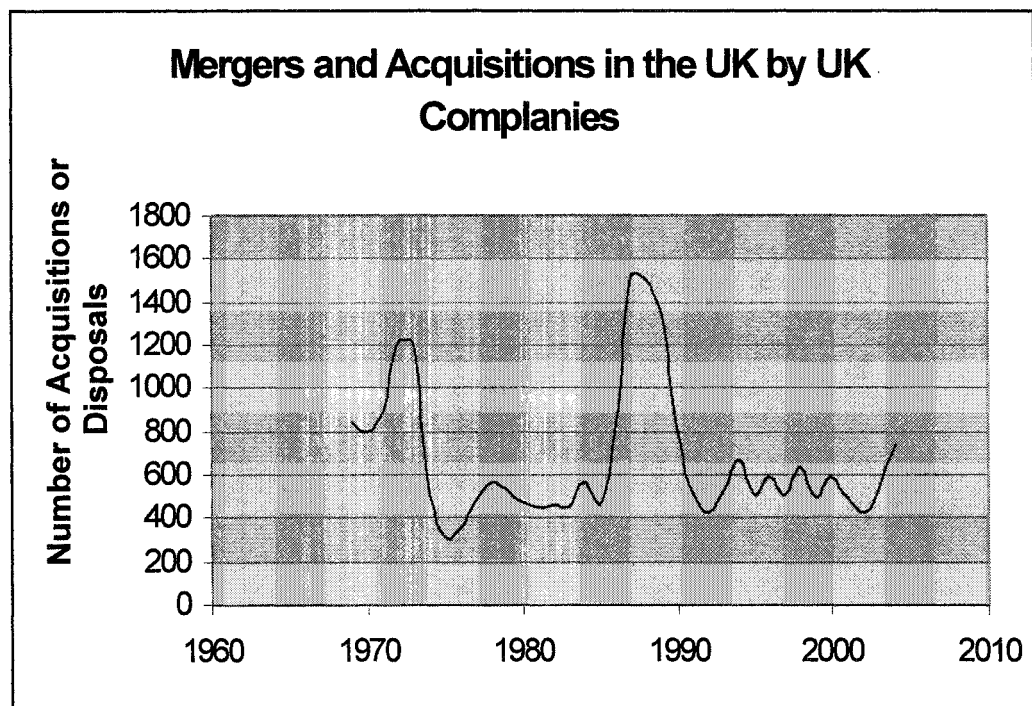
Looking at overall gain to the economy, the theoretical answer seems to be “yes” — assets are transferred from control of inefficient management to while empirical evidence for the UK shows that the merger and acquisition activity has a neutral effect on the economy and there are no extreme efficiency gains. (Watson & Head, 1998). McConell and Muscarella (1985) and Jarell, Lehn and Marr believe that investors analyzing mergers pay too much attention to short term earnings gains and don’t notice that these gains are at expense of long term prospects.. According to their study if investors . Some studies for the 1960s and 1970s showed that productivity declined in the years after an acquisition. But studies of the mergers activity in the 1980s (Healy et al., 1992) suggest there was a 2.4% increase in the companies’ pre-tax returns via to increase in turnover. On the other hand, it is argued that the merger wave of the 1980s led to companies being laden with debt and thus ill-prepared for recession. Then again, one could recall the Bain & Cy. Study of 50 largest bank acquisitions 1990-99 (cited in Schenk, 2000) and as far as can be inferred from the stock valuations only 30% can be classified as possible overall successes. Therefore overall gain to the economy is inconclusive.



## 2.6 Merger Waves

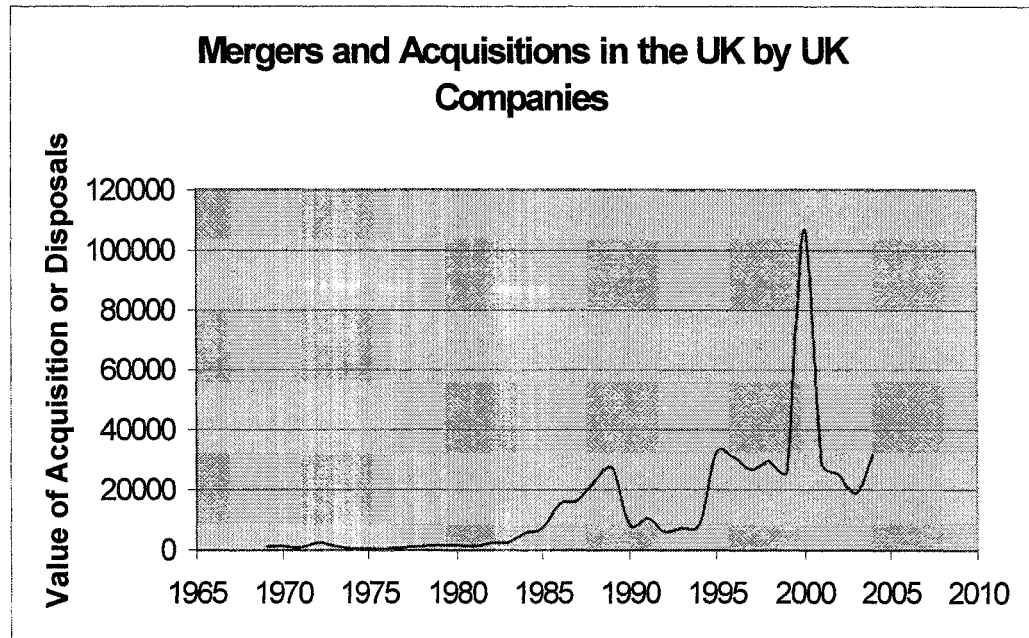
Merger waves are defined as “periods of time characterized by a relatively large number of mergers reported simultaneously in many industries” (Auster & Sirrower, 2002). The graphs below show the waves of takeover activity in the UK from 1969 to 2004.

**Figure 2.1: Mergers and Acquisitions in the UK by UK Companies (Number of Deals)<sup>1</sup>**



<sup>1</sup> Obtained from [statistics.gov.uk](http://statistics.gov.uk)

**Figure 2.2: Mergers and Acquisitions in the UK by UK Companies (Total Value of Deals)<sup>2</sup>**



The reasons for merger waves are not clearly identified. The first peak of merger waves started in 1968. Auster & Sirrower (2002, p. 217) suggest that “inexperience and uninformed reaction to uncertainty and change” and “Wow, grab it” are the cause of merger waves. Watson and Head (1998) also state that a merger wave in 1986 III –1989 IV started as a result of the Stock Exchange crash in 1987 leading to an increased ability for the companies to acquire debt. This wave involved conglomerate takeovers where companies were acquiring what they saw as under priced market entities.

<sup>2</sup> Obtained from statistics.gov.uk

The wave that occurred in mid 1990s, mostly involved horizontal acquisitions in certain industries, where companies were trying to obtain economies of scale and synergy (Head, 1998).

From the examined sources only Watson and Head (1998) link merger waves somehow to the deregulations in the capital markets, increase in funds available for borrowing etc. Brealey and Myers (2000) refer to the merger wave behavior as a “cascade” when each company adjust their own preferences according to the views of others and the rest of the sources find no reasonable explanation for it.

## ***2.7 Concluding Remarks***

Mergers and acquisitions are on the rise with the size and scope of deals escalating. Company executives seek to reduce annual expenses while creating ever more powerful operating and strategic synergies. Nevertheless, as consolidations have increased in volume, so too have the failures. Findings produced by empirical researchers attribute the failures primarily to non-integrated, incompatible cultures resulting in lost value and unattained synergies. At this stage it should be noted that the primary objective of this chapter is not to provide a detailed review of the literature in the area of corporate mergers and acquisitions, but an overview of the topic.

## **Chapter 3: The Market for Corporate Control, the Macroeconomic Activity and the Stock Market**

### ***3.1 Introduction***

The market for corporate control is continuously changing. The decades of 1980s and 1990s were marked by an extreme expansion in the takeover activity both in UK and abroad. Hughes (1993) and Boisi & Essig (1994) present a comprehensive review of mergers activity in UK and in USA respectively. Attempting to answer the fundamental question of why does the market for corporate control exist, both of them attempt to identify concrete links between the level of the mergers and acquisitions activity and the state of the economy. More specifically, Hughes (1993) employs a trade off model in order to assess the impact of mergers on the economy. Based on a static, partial equilibrium trade off, of allocative efficiency losses arising from merger related increases in market power, against any merger related cost efficiency gains arising from scale, from learning effects for the merging firms and from the reallocation of output between them and other firms of differing efficiency in the post-merger industry structure. However there are problems with this approach, namely that there is often a difference between social and cost benefits.

A quite similar approach is introduced by Fairburn and Geroski (1993). They suggest that when evaluating any merger or acquisition the central concern is the likely effect that such an activity will have on the performance of the entire industry. This is known as the “Structure – Conduct – Performance Theory”.

Moreover by reviewing some of the previous studies in which this theory tested they conclude that a non-linear, complex link does exist between the structure of the industry and the performance of the companies operating in this industry. The extension of the above conclusion is that it may be essential for a company to attempt an acquisition because of the circumstances it finds itself in.

On the other hand, Boisi and Essig (1994) suggest that the forces that drive the market for corporate control can be divided into asset and financing related components. Asset related forces involve the supply and demand for scarce strategic resources such as land, capital equipment, and managerial talent. On the other hand financing related forces include the level of real interest rates, the availability of equity and venture capital bank liquidity and credit environment, risk premiums, inflation and security market volatility. Both the asset and the financing related forces are the result of more fundamental elements of the business cycle. In other words macroeconomic factors such as fiscal and monetary policy, legal and regulatory regimes and technological changes affect the market and the business cycle which in turns simulates or retards the narrower asset or financing related forces and drive mergers and acquisitions.

Rock (1994) believes that there are several economic forces that influence the overall level of activity in the mergers and acquisitions field. More specifically, he argues that shifts in public sentiment are reflected in mergers marketplace, which by the 1990s was emerging from a brief period of severe gloom. However he fails to support his suggestions with strong empirical evidence.

Finally, Scherer (1988) suggest that two markets failure could be corrected by the proper functioning of a third one. In other words competition in production and input markets may fail to eliminate firms that are not minimizing costs and maximizing profits. Therefore the market for corporate control can be viewed as an essential occurrence that can be used to correct for such inefficiencies in other markets.

This chapter is designed to analyze the behaviour of the corporate control market in the UK during a period that incorporates excessive acquisitions activity in this country. More specifically, this chapter has three main objectives in studying further the characteristics of the aggregate mergers in the UK. First, it aims to determine formally the presence of mergers waves making use of the Markov switching models with no autoregressive dynamics and constant transition probabilities along the lines of Hamilton (1990) and applied by Engel and Hamilton (1990) in the context of exchange rates. These models have the capacity to capture abrupt changes in the evolution of a given time series. It extends existing research by using a Markov Switching Model, allowing the series to follow three regimes with different mean values enabling the series to be modeled using multiple time series representations. The three regimes defined here represent the series (1) in decreasing mergers activity periods at the end of a merger wave, (2) in normal mergers activity period, and (3) in rising mergers activity period at the beginning of a merger wave. Examining each of these different types of behavior provides a considerably more informative picture of the behavior of the series over time than has been

previously available. The dataset employed covers mergers activity in the UK from 1969:1 through 2003:4.

Second, it attempts to examine the relationship between the Mergers and Acquisitions activity in the UK with the Stock Market and the aggregate economic activity (Business Cycle). Finally, it is reasonable to consider that the relationship between the Mergers and Acquisitions activity, the Stock Market and the Business cycle might be significantly different during periods of falling, rising or stable Mergers activity.

The following of the chapter is organized in five sections: section 3.2 presents a review of the relevant literature; Section 3.3 describes the data and the methodology; Section 3.4 presents the empirical results for Markov switching model; Section 3.5 discusses the relationship between Mergers and Acquisitions activity in the UK with the Stock Market and the aggregate economic activity (Business Cycle). The final section provides a brief summary and some concluding remarks.

### ***3.2 Review of Literature***

#### ***3.2.1 Economic Effects and the market for Corporate Control***

An important question arises when studying acquisitions activity is why the market for corporate control exists. Although this question cannot be answered simply, an interesting suggestion is made by Scherer (1988). He specifically argued that two markets failure could be corrected by the proper functioning of a third one. Scherer (1988) believed that competition in production and input markets may fail to eliminate firms that are not minimising costs and maximising profits. Moreover he claimed that when the stock market operates in an efficient way, these firms would be removed automatically. Thus a market in corporate control is necessary for the efficient working of the economy as a whole, as it will remove those inefficient companies that the market fails to eliminate naturally. Scherer (1988) used Line of Business data collected by the Federal Trade Commission to create a sample of four hundred and seventy one American acquisitions between the years 1950 and 1976. Using ninety one firms for which data were available, he attempted to illustrate his hypothesis by examining changes in average profitability in the period before and after the acquisition. However, his results proved to be inconclusive on the subject of market efficiency and the author contended that, if takeovers existed to remove inefficient firms, post acquisition profits should exceed pre acquisition ones by a considerable margin. Nevertheless, this assumption was not confirmed by his results and Scherer fails to provide an adequate explanation.



Hughes (1993) also examined the effect of mergers on the economy using a trade off model. This model is based on the idea that there is a static partial equilibrium trade off between allocation efficiency losses and the cost-efficiency gains that appear after a takeover. He acknowledged that there are problems with this approach. More specifically, there is often a difference between social benefits and cost benefits. There are some effects that may induce further mergers which must be considered and the assumption of a self equilibrium economy with full employment, on which the static model is based, ignores the issues of investment, technical change, export preferences and employment effects which are also involved in the calculation of the social benefits of mergers and acquisitions activity. Consequently, the trade off model tends to produce results that use the issues of allocational efficiency as a proxy for monopolistic power. Hughes appeared to favour a quite similar approach to Scherer, namely that the control of a company can be visualised as a valuable asset independent of any other considerations. Under this perspective managerial efficiency is ensured by the “survival of the fittest”. This implicitly assumes that the bidding firms will always have efficient managers and the targets will comparatively have inefficient managers who will lose their jobs immediately after the completion of the acquisition. For this theory to work, the author claimed that a series of two assumptions must hold. Firstly, that the share price always reflects the expected profitability of the firm and that the bidders are able to identify the presence of inefficient management as distinct from unfavourable circumstances. Finally, the acquirer must be prepared to alter the wealth-maximising policies of a firm and be confident of making enough money in the post merger period in order to recover the cost of the

takeover. If these conditions do not hold, mergers are not generated by the efficiency argument and other justifications must be identified. Although Hughes did not test the above empirically, seems to believe that an examination of the benefits generated for the different parties in the merger and acquisition process will make the fundamental accuracy of this statement apparent.

A similar theory was advanced by Fairburn and Geroski (1993). The two authors contended that when evaluating any merger or acquisition the central concern is the likely effect that such an activity will have on the performance of the entire industry. They called this idea the “Structure – Conduct – Performance Theory”. This stated that the performance of the companies within the industry can alter the conduct of the other firms and ultimately change the structure of that industry. Fairburn and Geroski(1993) begun by reviewing a number of previous studies that attempted to test this theory. The results of these studies agree with Fairburn and Geroski’s conclusion that a link does exist between the structure of the industry and the performance of the companies operating in that industry. The link appears to be non linear, complex and rather weakly defined but Fairburn and Geroski were in no doubt that it exists. Clearly any factor that dramatically affects the market share of a firm will have a substantial effect on the profits of that company. The most obvious example of these factors is a horizontal acquisition. If this is correct then it suggests that mergers and acquisitions can alter the profits of all the companies within a certain industry simply by altering the market shares of one or two firms. This idea can also be taken in reverse and, in this case, it states that if the behaviour of a few firms can alter an industry then the nature of the industry can

obviously have an impact upon the actions of the firms within it. The extension of this idea is that it may be essential for a company to attempt an acquisition because of the circumstances that it finds itself in.

This leads on, naturally, to consider the impact of the economy on the market for corporate control. If the corporate control market can alter the way that the stock market functions as Fairburn and Geroski clearly believed, then it is very likely that the behaviour of the economy as a whole will have a considerable effect on the level of mergers and acquisitions activity. This point was discussed at length by Rock (1994). Rock believed that there are several economic forces that influence the overall level of activity in the mergers and acquisitions field. He named five and attempted to provide brief explanations of their importance and effect. The first of these is the economic outlook which, the author argued, is probably the most important economic influence on takeover activity. Rock maintained that if the economic outlook is promising and people are optimistic, activity in the market for corporate control will increase significantly. He illustrated this point with the example of USA in the early 1990's. This economy was actually one of the fastest growing in the world at that time but the market was depressed with a noticeable lack of consumer enthusiasm or confidence. As a result the acquisition market was noticeably depressed compared to the confident times in 1980's. Whilst the country and the people involved in the stock market were not feeling conspicuously confident about their economic future, the enthusiasm for mergers and acquisitions were negligible. The second one of Rock's economic factors that can have an impact on mergers and acquisitions activity is the availability of

financing alternatives. No acquisition, however beneficial, can progress beyond the planning stage without adequate financing. It is important, then, to consider the availability of funds to those involved and the alternatives that they have. If there are limited funds available to the acquiring companies then they are going to have to consider either retaining earnings or borrowing the necessary funds which may prove to be prohibitively expensive especially when the market as a whole is depressed. The next point is concerned with the balance between the offer made by the bidding firms and the target shareholders' expectations for their company. If the shareholders think that the value of the stock is going to move up significantly in the future then they may not want to sell now, irrespective of the premium the acquiring firm is prepared to offer. The fourth point in this paper refers to the strategic challenges produced by the continually changing face of the business world. The laws governing mergers and acquisitions are permanently in review in different countries around the world and so the potential acquirer must endeavour to stay abreast of these changes and understand how they might affect any planned takeovers. Finally there is the reputation of mergers and acquisitions. If the corporate control market is not popular for some reasons then the practitioners will find it harder to complete their deals. Under this situation, funding will be more difficult to come by and the shareholder of the bidding company unwilling to take the risk of acquiring another firm. It is unfortunate that Rock had no empirical evidence to provide in support of his conclusions but the rationale behind his approach is quite clear and he succeeded to make a persuasive argument for believing that the economic climate must have a significant effect on the functioning of the market for mergers and acquisitions.

Having reviewed these articles on the nature of the mergers and acquisition market in general terms it seems that the corporate control market can be viewed both as an essential occurrence that can be used to correct for potential inefficiencies in other markets and as a less important event that can be triggered by a certain conjunction of external effects.

### **3.2.2 *Merger Waves***

Studies in the area confined themselves to limited descriptive characterizations of the stochastic process behind merger data either by restricting attention to linear time series models or by devising limited test for wave patterns.

The early literature in the area can broadly be divided into two categories. Firstly there are papers using time series methodologies found in general that acquisition activity is random and therefore unpredictable. Shugart and Tollison (1984) found that numbers of acquisitions are best described by a random walk and declared that this meant that the series was random. They examined the number of acquisitions that occurred in the USA in each of two periods, 1895 to 1920 and 1947 to 1979. The conclusion of their study was that the behaviour of the corporate control market is best described by a white noise process and cannot be linked to the behaviour of the economy. This result provides the first hypothesis that will be tested in the empirical section of this chapter, that acquisitions numbers are random. If this hypothesis is rejected then the level of acquisitions activity can be deemed to be predictable as the vast majority of

empirical papers in the area found. In particular, these papers linked the number of acquisitions to the economic environment. Furthermore Chowdhury (1993) used unit root tests to show that the changes in mergers number are random although he did not investigate levels of mergers activity. However, Golbe and White (1993) observed that Shugart and Tollison (1984) appear to have confused the analysis of acquisitions level with that of differences and their final conclusion actually imply that, whilst differences are random, takeovers levels are autoregressive.

The second group of literature concentrated on the influence that macroeconomic factors have on takeover activity levels. In one of the very first papers in the area Gort (1969) found concrete links between the economic conditions and the level of acquisitions activity. More specifically, he proposed that acquisitions take place because the economic conditions change in such a way that the values of the firms were significantly altered. Gort (1969) considered roughly six hundred American acquisitions that occurred between 1951 and 1959 and attempted to show that these acquisitions took place because the economic conditions changed in such a manner that affected positively the values of the firms.

Following Gort (1969), Steiner (1975) attempted to link the level of activity in the corporate control market to specific macroeconomic factors, such as stock prices and GNP. He used a multivariate regression to model the number of acquisitions that occurred between 1949 and 1971 using economic cycle

variables. This study incorporated other terms such as interest rates, but none of them proved to be significant.

At a later stage Melicher, Ledolter and D'Antonio (1983) proposed their “merger activity – economic prosperity” theory which links changes in the expected level of economic growth and the capital market conditions to acquisition levels. This theory states that changes in the expected level of economic growth and the capital markets can generate conditions where the financing of an acquisition is far simpler than in other periods. Consequently, these factors can be linked to the level of acquisition activity and the two authors attempted to demonstrate this by applying multivariate regression models. Their empirical results supported the supposition concerning the link between capital markets and acquisitions numbers but were inconclusive on the relationship between the level of expected economic growth and the number of takeovers.

On the other hand Golbe and White (1988) demonstrated that the behaviour of the corporate control market is not random and then proceeded to analyse the link between the level of takeovers in the USA and the economic situation. The data set used in this paper covers the period from the middle of 1940's to 1985. According to their findings there is a positive link between GDP and acquisitions level whilst a negative relationship exist between the number of takeovers and interest rates.

A more promising line of research is the adoption of non-linear models that naturally accommodate the notion of discrete shifts associated with merger waves. Town (1992), Linn and Zhu (1997) and Resende (1999) attempt to explain the USA aggregate merger activity by two different autoregressive processes that co-exist in one model. Both processes are simultaneously present in two different states or regimes representing the “normal merger activity” and “merger wave periods” respectively. The transition between these two states is governed by a first order Markov process, with a probability of each state occurring determined by each observation.

Town (1992) seeks to answer two questions regarding the aggregate behaviour of mergers. More specifically, he attempts to investigate what type of univariate time – series structure best characterizes the merger data, and whether this structure can account for wave behaviour. Moreover he tries to find out when exactly merger wave occurred, given that, from a statistical point of view, they are structural events. He analyses the linear and non-linear time-series behaviour of five mergers and acquisitions data set, which span most of the twentieth century. Most specifically, several standard diagnostic tests are used to examine the forecast errors from the different models, fitted to the merger data. If the data were truly generated from the fitted model the forecast errors should be white noise. In particular, if the data generated from a non-linear model, a fitted linear model should leave extra structure in the residuals. He tests for this additional structure using a statistic proposed by Brock, Dechert and Schienkman (1987). According to his empirical findings linear models fail to capture all of the structure of the data. Aggregate merger behaviour is well



described by a non-linear, Markov Switching regime model. Mergers and acquisitions alternate between two states: a high mean and a high variance state and a low mean and a low variance state. In other words, in a univariate framework merger waves appear to be an endogenous phenomenon. Linn and Zhu (1997) fit an MS model with two identical first-order autoregressive components to untransformed USA data and their concatenated series. They also find strong results for their MS model with respect to all their series (numbers and real values of mergers).

More recently, Resende (1999) investigates the behaviour of mergers and acquisitions in the UK at the sectoral level, making use of the Markov switching model with no autoregressive dynamics and constant transition probabilities along the lines of Hamilton (1990) and applied by Engel and Hamilton (1990) in the context of exchange rates. According to his empirical findings M&A appear to display analogous behaviour to the 'long swings' in the exchange rate literature. However the incidence of M&A waves is not exactly the same, although there are some similarities. Moreover the random walk specification is strongly rejected.

Finally, Gartner and Halbheer (2006) investigate the merger wave hypothesis for the UK and the USA, using quarterly data for the last thirty years employing a two state Markov Switching model. Their empirical findings suggest for the USA the beginning of a merger wave in the mid 1990s but not the much discussed 1980s merger wave. As opposed to the USA, mergers in the UK

exhibit multiple waves, with activity surging in the early 1970s and the late 1980s.

Furthermore, most of these studies applied the Hamilton (1989) smoother to identify and date the merger waves. Their estimated probabilities of the process being in a wave state confirm the established merger wave dates. These results suggest that aggregate mergers activity in the USA behave as if they are generated by such a model. This has important methodological implications for research into the determinants of merger activity. A discrete two-state Markov switching process that allows for regime switching behaviour to be generated endogenously provides a unique framework for detecting the causes of these regime changes, or transitions between normal merger activity and merger waves. These applications allow us to greater insight in that they provide us with a probabilistic inference on the separation between normal activity and waves and the dynamics of transition between the two can be quantified and thus explained.

### ***3.3 Data and Methodology***

#### ***3.3.1 Introduction***

Simple econometric techniques, such as cross-sectional regression models, have failed to generate a consistent model for merger waves. The next logical methodological step is the estimation of linear time series models, such as autoregressive or moving average processes. This technique simply involves

transforming the data into a stationary series and then identifying a time-series model for the data using a set of criteria to ensure that the model is a good fit. Once the model has been identified, it is relatively simple to analyze the data or to attempt to predict the future values of the series. Models of this type have many advantages because they are relatively simple to implement but, obviously, cannot be used to replicate the behaviour of a non-linear series.

The failure of past models for acquisition activity to adequately replicate the behaviour of the data suggests that it may be non-linear and should be modelled accordingly. Many series do exhibit non-linear behaviour over time and there are several methods of analysis that are capable of dealing with this characteristic. Of particular interest here are those models devised to deal with data that displays very different behaviour over time. This leads to the use of a non-linear time-series model in this chapter, specifically a regime switching model.

Regime switching models are often used to represent non-linear data by splitting the series into a finite number of regimes, each of which is characterized by a linear equation. The structure of the process remains unchanged across regimes but the parameters differ in each case. Movement between the regimes is determined by a regime variable.

### 3.3.2 *Hamilton's Model of the USA Business Cycle*

In his original model Hamilton (1989), contractions and expansions of the business cycle are modelled as switching regimes of the stochastic process generating the growth rate of real output  $\Delta y_t$ :

$$\Delta y_t - \mu(s_t) = \alpha_1 (\Delta y_{t-1} - \mu(s_{t-1})) + \dots + \alpha_4 (\Delta y_{t-4} - \mu(s_{t-4})) + u_t \quad (3.1)$$

In (3.1) the two regimes are associated with different conditional distributions of the growth rate of the real output, where the mean growth rate  $\mu$  depends on the state or regime  $s_t$ . For a meaningful business cycle model the mean should be negative in the first regime  $\mu_1 < 0$  (recession), and positive in the second,  $\mu_2 > 0$  (expansion). The variance of the disturbance term  $u_t \sim \text{NID}(0, \sigma^2)$ , is assumed to be the same in both regimes.

The stochastic process generating the unobservable regimes is an ergodic Markov chain defined by the constant probabilities:

$$p_{12} = \Pr(\text{recession in } t \mid \text{expansion in } t-1),$$

$$p_{21} = \Pr(\text{expansion in } t \mid \text{recession in } t-1).$$

The transition probabilities are estimated together with the parameters of equation (3.1).

By inferring the probabilities of the unobserved regimes conditional on the available information set, it is possible to reconstruct the regimes and to date the turning points of the time series under consideration (business cycle in Hamilton, 1989). Hamilton (1989) demonstrated that the model is able to track

the NBER reference cycle very closely. This suggests that the Markov switching approach should also be useful for the modelling and dating of time series that explore similar behaviour.

### 3.3.3 Markov Switching Vector Autoregressive Models

Like other regime switching models, the Markov switching vector autoregressive model (MS-VAR) is a vector autoregressive process of the observed time series vector  $y_t = (y_{1t}, \dots, y_{Kt})'$ , whose parameters are, at least partly, unconditionally time-varying but constant when on an unobservable discrete regime variable  $s_t \in \{1, \dots, M\}$ :

$$y_t - \mu(s_t) = A_1(s_t)(y_{t-1} - \mu(s_{t-1})) + \dots + A_p(s_t)(y_{t-p} - \mu(s_{t-p})) + u_t \quad (3.2)$$

Where  $u_t$  is the Gaussian error term conditioned on  $s_t$ :  $u_t | s_t \sim NID(0, \Sigma(s_t))$ . A p-th order, M-state Markov switching vector autoregressive model of a K dimensional time series vector is denoted MS(M)-VAR(p). The parameter matrix shift functions  $\mu(s_t)$ ,  $A_1(s_t)$ , ...,  $A_p(s_t)$  and  $\Sigma(s_t)$  describe the dependence of the VAR parameters  $\mu$ ,  $A_1$ , ...,  $A_p$  and  $\Sigma$  on the regime variable  $s_t$  as in:

$$\begin{aligned} \mu_1 &= (\mu_{11}, \dots, \mu_{K1})' & \text{if } s_t = 1, \\ &\vdots & \\ &\vdots & \\ &\vdots & \\ \mu_M &= (\mu_{1M}, \dots, \mu_{KM})' & \text{if } s_t = M. \end{aligned} \quad (3.3)$$

The decisive characteristic of a Markov switching vector autoregressive model is that the unobservable realizations of the regime  $s_t \in \{1, \dots, M\}$  are generated by

a discrete time, discrete state Markov stochastic process, which is defined by its transition probabilities:

$$p_{ij} = \Pr(s_{t+1} = j \mid s_t = i), \quad \sum_{j=1}^M p_{ij} = 1 \text{ for all } i, j \in \{1, \dots, M\}. \quad (3.4)$$

It is usually assumed that the Markov process is irreducible and ergodic.

In the model (3.2) there is an immediate one time jump in the process mean after a change in the regime. Frequently, it is more plausible to assume that the mean smoothly approaches a new level after the transition from the one state to another. In such a situation, the following model with a regime dependent intercept term  $\nu(s_t)$  could be used:

$$y_t = \nu(s_t) + A_1(s_t)y_{t-1} + \dots + A_p(s_t)y_{t-p} + u_t. \quad (3.5)$$

In contrast to linear time varying VAR models, the mean adjusted form (3.2) and the intercept form (3.5) are not equivalent. They imply different dynamic adjustments of the observed variables after a change in regime. While a permanent regime shift in the mean  $\mu(s_t)$  causes an immediate jump of the observed time series vector onto its new level, the dynamic response to the once-and-for-all regime shift in the intercept term  $\nu(s_t)$  is identical to an equivalent shock in the white noise series  $u_t$ .

The MS-VAR model allows for a great variety of specifications. In principle, it would be possible to alternate the specification of the regime generating process (i) by making all parameters time varying and (ii) by introducing separate regimes for each equation (or even for each parameter). But this is not a

practical solution as the number of parameters of the Markov chain grows quadratic in the number of regimes and coincidentally shrinks the number of observations usable for the estimation of the regime dependent parameters. For the above described reasons it is preferable to impose the assumption of a common regime variable generating simultaneously regime shifts in all equations of the system, i.e. identical break points for all variables and parameters, and also to restrict the number of regime dependent variables .

In empirical research, only some parameters will be conditioned on the state of the Markov chain while the other parameters will be regime invariant. In order to establish a unique notation for each model, Krolzig (2003) specifies with the general MS(M) term the regime dependent parameters:

- M     Markov switching *mean*,
- I     Markov switching *intercept*,
- A     Markov switching *autoregressive parameters*,
- H     Markov switching *heteroscedasticity*.

The MS-VAR model provides a very flexible framework which allows for heteroscedasticity, occasional shifts, reversing trends and forecasts performed in a non-linear manner. In Mergers and Acquisitions analysis, the focus is on models where the mean (MSM(M)-VAR(p) models) is subject to occasional discrete shifts creating episodes of increasing or decreasing mergers activity.

### 3.3.4 MS-VAR Models of Mergers and Acquisitions Activity

More formally, we define a stationary series  $\Delta y_t$  as being conditional on a regime variable,

$$s_t \in \{1, 2, \dots, M\}$$

in the manner typified by equation 3.6.

$$p(\Delta y_t | Y_{t-1}, X_t, s_t) = \begin{cases} f(\Delta y_t | Y_{t-1}, X_t, \theta_1) & \text{if } s_t = 1 \\ f(\Delta y_t | Y_{t-1}, X_t, \theta_2) & \text{if } s_t = 2 \\ \dots & \\ f(\Delta y_t | Y_{t-1}, X_t, \theta_M) & \text{if } s_t = M \end{cases} \quad (3.6)$$

where

$$p(\Delta y_t | Y_{t-1}, X_t, s_t)$$

is the probability density function of the vector of endogenous variables

$$\Delta y_t = (\Delta y_{1t}, \Delta y_{2t}, \dots, \Delta y_{Et})'$$

which, in turn, is conditional on the past behaviour of the process,

$$Y_{t-1} = \{\Delta y_{t-i}\}_{i=1}^{\infty}$$

some exogenous variables

$$X_t = \{x_{t-i}\}_{i=1}^{\infty}$$

and the regime variable  $s_t$ . The term  $\theta_m$  represents the parameter vector when the series is in regime  $m$ , where  $m = 1, \dots, M$ .



For a full description of the process  $\Delta_{yt}$ , it is also necessary to specify the stochastic process,  $s_t$ , that defines the regime, as in equation 3.7.

$$\Pr(s_t | Y_{t-1}, S_{t-1}, X_t; \rho) \quad (3.7)$$

where  $S_{t-1}$  represents the history of the state variable and  $\rho$  is a vector of parameters of the regime generating process.

In many cases the regime variable cannot be observed and the historical behaviour of the series must be inferred from the actual behaviour of the process. The appeal of this approach is that the historical behaviour of the series,  $\Delta_{yt}$ , does not determine the regime in any way - that is left entirely to the regime variable,  $s_t$ . However, there are also instances in which the switching variable cannot be observed, especially when there are multiple regime changes and this can be problematical. To circumvent this issue, a Markov chain is often used for the switch. This is a simple system that represents the probability of changing state in the future.

Using a first-order Markov chain specification, the regime variable is assumed to take only integer values  $\{1, 2, \dots, M\}$  and the probability of  $s_t$  taking any value is dependent only on its previous value. Thus, the Markov chain represents the probability that the system will be in a particular state in the next time increment, conditional on the current state of the system, as in equation 3.8.

$$\Pr(s_t | Y_{t-1}, S_{t-1}, X_t; \rho) = \Pr(s_t | s_{t-1}; \rho) \quad (3.8)$$

This relationship is linked to the transition probabilities

$$p_{ij} = \Pr(s_{t+1} = j | s_t = i)$$

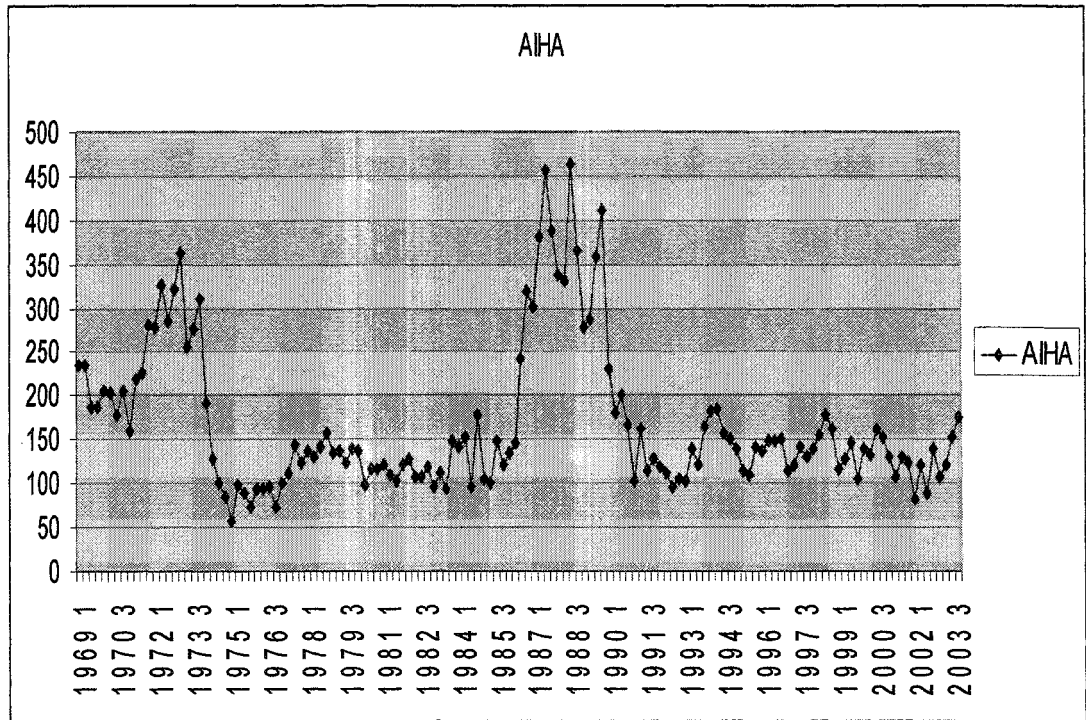
which are often represented as a transition matrix of the form given in equation 3.9.

$$P = \begin{bmatrix} p_{11} & p_{12} & p_{13} & \dots & p_{1J} & \dots & p_{1M} \\ p_{21} & p_{22} & p_{23} & \dots & p_{2J} & \dots & p_{2M} \\ p_{31} & p_{32} & p_{33} & \dots & p_{3J} & \dots & p_{3M} \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ p_{J1} & p_{J2} & p_{J3} & \dots & p_{JJ} & \dots & p_{JM} \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ p_{M1} & p_{M2} & p_{M3} & \dots & p_{MJ} & \dots & p_{MM} \end{bmatrix} \quad (3.9)$$

This multi-regime framework allows the series to display different characteristics at different times and to move between these regimes from period to period. Modeling time series data in this way allows for some potentially very informative results to be generated in cases when the data seems to display several different types of behaviour over time.

In this chapter, the data represents the total number of mergers and acquisitions in the UK between the beginning of 1969 and the end of 2003, reported on a quarterly basis. The data is from the UK Office of National Statistics (ONS) and is limited to completed deals only. Even the most superficial examination of the series of acquisition numbers is sufficient to reveal that this is clearly not a series that behaves in a conventional manner, as Figure 3.1 demonstrates. The most striking features of the data series are the two periods of excessive activity (merger waves) that occur within the sample period. The majority of the series is characterized by the stable periods, typified by relatively small changes between observations. In addition to this stable regime, there are also periods of explosive growth and dramatic falls that denote the beginning and end of the merger waves and these also need to be taken into consideration.

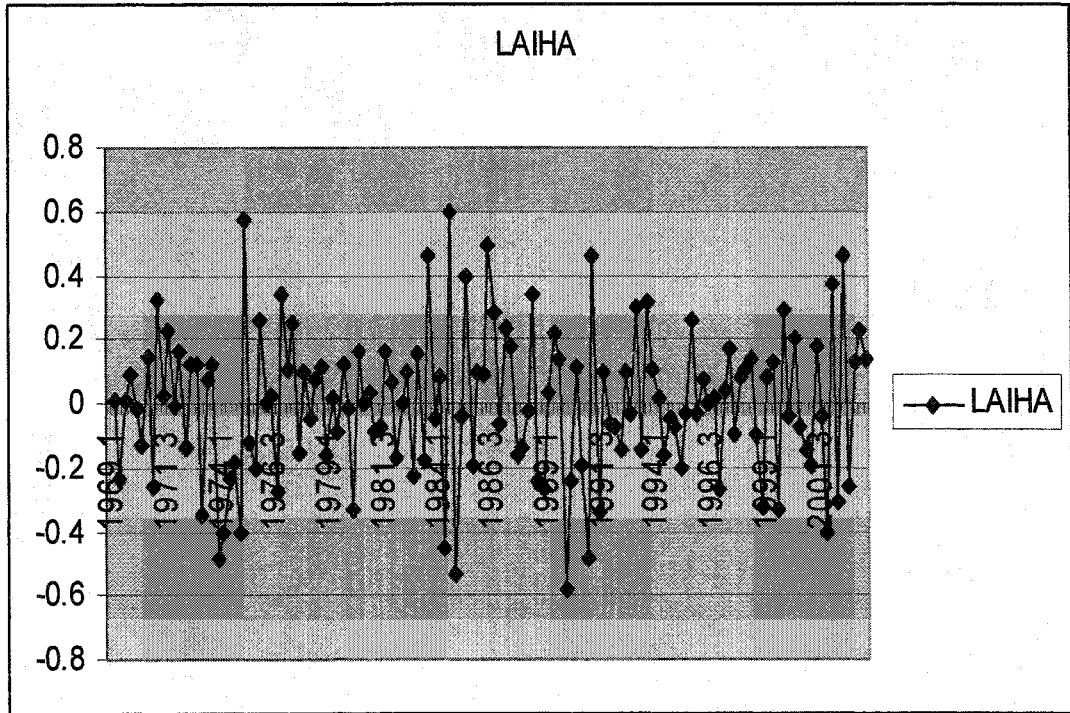
**Figure 3.1: Mergers and Acquisitions in the UK 1969 - 2003**



The data is  $I(1)$ <sup>1</sup> and strongly autoregressive with the first and fourth lags being particularly important. Given that the data used here is quarterly, this result is not unexpected. Figure 3.2 represents the data after making it stationary.

<sup>1</sup> Augmented Dickey – Fuller (ADF) Test for stationarity generated a probability of 0.3450, higher than 0.05, so the null hypothesis of a Unit Root is not rejected at 5% level of significance.

**Figure 3.2: Mergers and Acquisitions in the UK 1969 – 2003 (Logged Values)**



Using the Markov Switching model over three regimes, this data will be modelled as an autoregressive process of order 4 which is typified by equation 3.10.

$$\Delta y_t = \nu_m + \theta_{m1}\Delta y_{t-1} + \theta_{m2}\Delta y_{t-2} + \theta_{m3}\Delta y_{t-3} + \theta_{m4}\Delta y_{t-4} + \varepsilon_t, \quad \varepsilon_t \sim IID(0, \sigma_m^2) \quad (3.10)$$

The transition matrix will be of the form given in equation 3.11.

$$P = \begin{bmatrix} p_{11} & p_{12} & p_{13} \\ p_{21} & p_{22} & p_{23} \\ p_{31} & p_{32} & p_{33} \end{bmatrix} \quad \text{where } p_{i3} = 1 - (p_{i1} + p_{i2}) \text{ for } i = 1, 2, 3 \quad (3.11)$$

### 3.4 Empirical Results

The results reported here are all generated using Ox version 3.2<sup>2</sup> (Doornik, 2002) and MSVAR<sup>3</sup> version 1.31e (Krolzig, 2003). The results support the hypothesis that there are three distinct regimes in the series. A likelihood ratio (LR) test rejects the possibility of fitting a linear model to the series and this result remains true when the test is adjusted in the manner advocated by Davies (1977, 1987). The test proposed by Davies is a modified form of the LR test which gives a corrected upper bound for the probability value. (For a clear and concise description of the test devised by Davies, see Garcia and Perron, 1996).

The model diagnostics are illustrated in Figure 3.3 and they suggest that the model is generally well-specified. There is a slight problem with serial correlation in the standardized residuals but this problem does not extend to the

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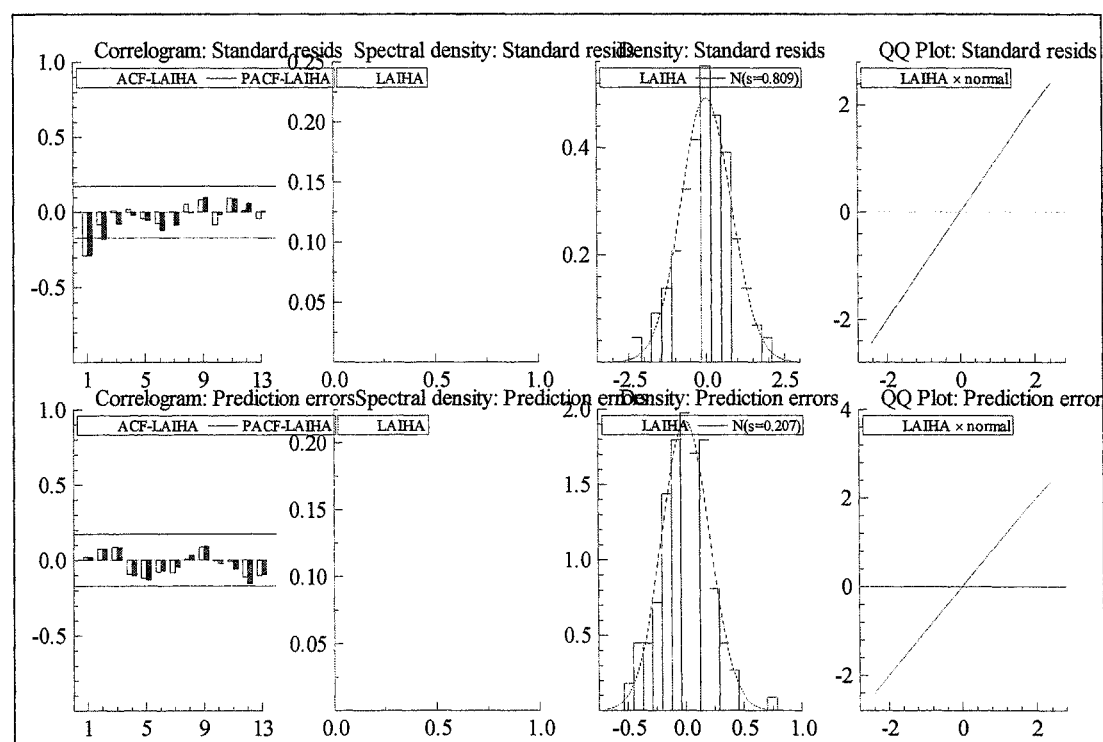
<sup>2</sup> **Ox** is an object-oriented statistical system. At its core is a powerful matrix language, which is complemented by a comprehensive statistical library. Among the special features of Ox are its speed, well-designed syntax and editor, and graphical facilities. Ox can read and write many data formats, including spreadsheets and OxMetrics files; Ox can run most econometric Gauss programs.

<sup>3</sup> **MSVAR** is an **Ox** package designed for the econometric modelling of univariate and multiple time series subject to shifts in regime. It provides the statistical tools for the maximum likelihood estimation (EM algorithm) and model evaluation of *Markov-Switching Vector Autoregressions* as discussed in Krolzig (1997). A variety of model specifications regarding the number of regimes, regime-dependence versus invariance of parameters etc. provides the necessary flexibility for empirical research and will be of use to econometricians intending to construct and use models of dynamic, non-linear, non-stationary or cointegrated systems.

**MSVAR** can be used by writing a small Ox program. Ox is an object-oriented matrix language with a comprehensive mathematical and statistical function library. As **MSVAR** derives from the Modelbase class, it allows the easy use and exchange with other classes such as PcFiml. In conjunction with Ox Professional, **MSVAR** can be used interactively via the user-friendly interface OxPack in combination with GiveWin 2 for data input and graphical and text output.

predictive errors, which all lie comfortably within the standard error bands. The density and QQ plots both suggest that the model is well-specified, as they are very close to normal distributions for both the standardized residuals and the predictive errors.

**Figure 3.3: Model Diagnostics**



The estimated coefficients for this model are given in Table 3.1.

**Table 3.1: Estimated Parameters from the Three Regimes for UK M&As 1969-2003**

<i>Regime Dependent Mean Values</i>	
$v_1$	-0.3238 (-6.7917) ***
$v_2$	-0.0347 (-5.6830) ***
$v_3$	-0.2047 (5.1568) ***
<i>Autoregressive Coefficients <math>\theta_{im}</math></i>	
$\Delta y_{t-1}$	-1.1395 (-9.7562) ***

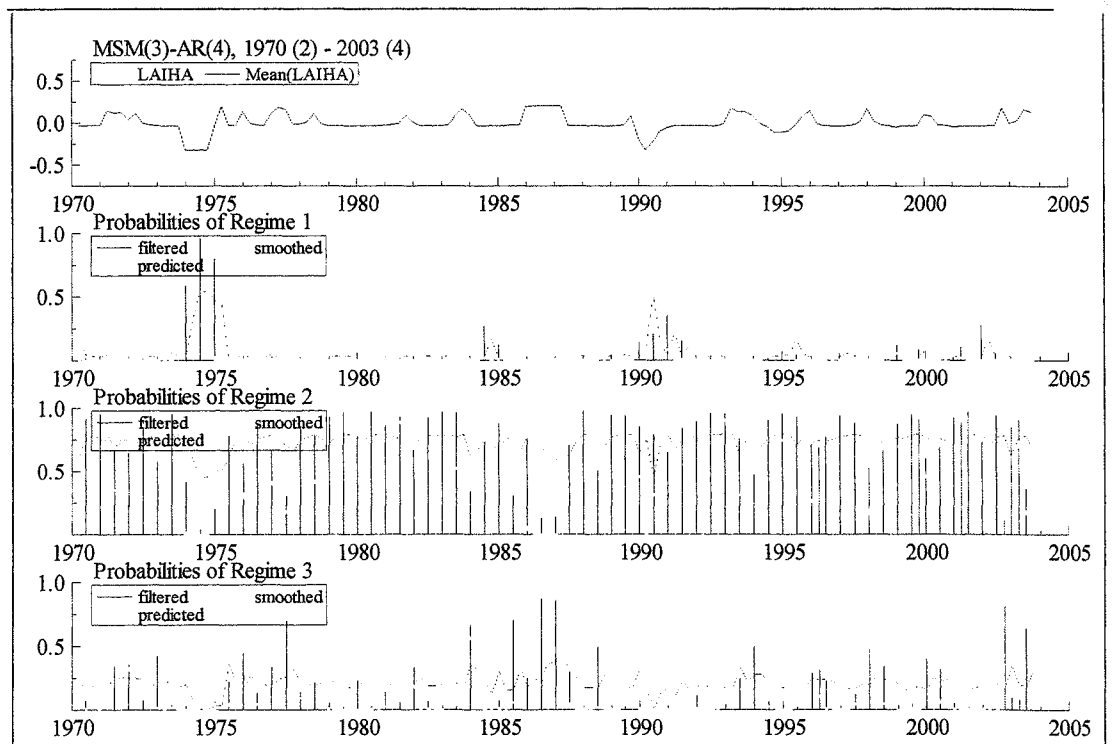
$\Delta y_{t-2}$	-1.0711 (-6.8740) ***
$\Delta y_{t-3}$	-0.7426 (-5.1299) ***
$\Delta y_{t-4}$	-0.1970 (-2.893) *

\*\*\*, \*\*, \* Denotes significance at 1%, 5% and 10% respectively

The mean values are clearly different and statistically significant at 1% level of significance, supporting the hypothesis that the series follows three distinct regimes over the sample period and the coefficients on the four lags are all statistically significant. The transition matrix for these regimes is given as equation 3.12 and the regime probabilities are illustrated in Figure 3.4.

$$P = \begin{bmatrix} p_{11} & p_{12} & p_{13} \\ p_{21} & p_{22} & p_{23} \\ p_{31} & p_{32} & p_{33} \end{bmatrix} = \begin{bmatrix} .5589 & .4411 & .4.099 \ e - 009 \\ .02590 & .8010 & .1731 \\ .022741 & .5879 & .3847 \end{bmatrix} \quad (3.12)$$

**Figure 3.4: Regime Probabilities**



In these results, Regime 1 represents the periods in which the series is dropping sharply at the end of a merger wave, Regime 2 represents the more stable periods in between the increases and decreases and, finally, Regime 3 represents the periods in which the series is rising rapidly as a merger wave develops.

When the series is in Regime 1 it is most likely to remain in that regime (55.89%), although the probability of the series flattening out and moving to Regime 2 is almost as likely (42.96%). There is virtually no chance of the series changing directly from Regime 1 to Regime 3.

The dominant regime is clearly Regime 2, which could be described as the normal behaviour of the series; the period in which the merger waves do not exist. The probability that the series will remain in Regime 2, given that it is currently there, is high (80.1%). If the series deviates from Regime 2, it is more likely to move to Regime 3 (17.31%), than Regime 1 (2.59%), but neither of these changes has a particularly high probability. Finally, when the series is rising (Regime 3), it is most likely to return to the stable behaviour typified by Regime 2 (58.79%) and this is the only instance in which the data is more likely to change regime rather than remain where it currently is. If the data does not return to Regime 2, it is most probable that it will continue in Regime 3. The probability of a change to Regime 1 is most unlikely (2.741%).

In addition to the transition probabilities, the expected duration for each of these regimes can also be calculated and appears in Table 3.2.



**Table 3.2: Durations of the Three Regimes Regimes for UK M&As 1969-2003**

	Number of Ergodic		
	Observations	Probability	Duration
Regime 1	7.6	0.0561	2.27
Regime 2	99.5	0.7367	5.03
Regime 3	27.9	0.2072	1.63

The durations confirm the information supplied by the transition probabilities. The expected duration of Regime 2 is considerably longer than the durations of either of the other two regimes, and the majority of the data demonstrates this more stable behaviour. When considering Regimes 1 and 3, it is clear that the drops tend to last longer than increases, as indicated by the longer expected duration for Regime 1.

There have been suggestions that merger waves are analogous to bubbles as they are both phenomena in which the data rises above the fundamental value of the series. As with a bursting bubble, the merger wave ultimately ends and the series returns to the more normal level of activity. With a rational bubble, the time that the series takes to return to its fundamental value is usually considerably shorter than the time spent rising at the start. Here, the opposite is true and the creation of the merger wave is more dramatic than the end. This is somewhat unexpected and merits some further analysis, so more tests are carried out here to investigate the behaviour of the data in these periods.

Following work on business cycle asymmetry by Clements and Krolzig (2003), tests are conducted to determine whether the increases and decreases in the

series of merger waves are symmetric or not. The first test is for “sharpness”, or asymmetry, in the peaks and troughs of the data. This test evaluates whether the peaks and troughs are similar in nature, or if one is more rounded and the other sharper. The null hypothesis in this test is that there is no difference in the turning points and this is tested by determining whether the transition probabilities to and from the outer regimes are the same. For the three regime model estimated here, accepting the null hypothesis jointly requires  $p_{13}=p_{31}$ ,  $p_{12}=p_{32}$  and  $p_{21}=p_{23}$ . Given the nature of the merger and acquisition data, it is unlikely that the null hypothesis will be rejected in this test.

The second test is for “deepness” which determines whether the amplitude of the troughs is substantially different to the amplitude of the peaks and, as before, the null hypothesis is that there is no difference. This is a form of Wald test and is based on an evaluation of the skewness of the data. Once again, given the fact that merger waves appear to represent a temporary deviation in the series away from its normal value, it is reasonable to expect that this null hypothesis will also be accepted.

Finally, there is the test for “steepness” which investigates the possibility that the movement of the series in one direction is significantly steeper than in the other direction. This is the most pertinent of these tests in relation to the merger and acquisition data. The null hypothesis is that there is no difference in the steepness but, following the analysis of the regime durations, it is expected that this hypothesis will be rejected for this data.

The results for these three tests reported in Table 3.3 and match our expectations. There is no evidence of differences in the sharpness or deepness of the periods in which the merger waves start and fall but there is evidence of significant differences in the steepness with which the waves begin and end. The null hypothesis of no difference in steepness is rejected at the 5% level, which supports the earlier supposition that merger waves begin more rapidly than they end.

**Table 3.3: Tests of Asymmetry Regimes for UK M&As 1969-2003**

<i>Test</i>	<i>Calculated Value</i>
<b>Sharpness Test</b>	4.7849
<b>Deepness Test</b>	0.2989
<b>Steepness Test</b>	4.6137**

\*\*\*, \*\*, \* Denotes significance at 1%, 5% and 10% respectively

The next step is to identify the specific dates for regimes 1, 2 and 3. In Markov-switching models, the classification and the dating of the regimes amounts to assigning every observation  $y_t$  to a given regime  $m=1, \dots, M$ . The rule that is applied here is to assign the observation at time  $t$  according to the highest smoothed probability, i. e.:

$$m^* = \arg \max_m Pr(s_t = m | Y_T)$$

At every point in time, a smoothed probability of being in a given regime is calculated (the inference is made using the whole set of data points), and this observation will be assigned to a given regime according to the highest smoothed probability. The following table presents the results.

**Table 3.4: Regime Classification Regimes for UK M&As 1969-2003**

Regime 1	Months Duration	Regime 2	Months Duration	Regime 3	Months Duration
1974:1 - 1974:4	12	1970:2 - 1971:1	12	1971:2 - 1971:4	9
1990:1 - 1990:3	9	1972:1 - 1972:1	3	1972:2 - 1972:2	3
		1972:3 - 1973:4	15	1975:2 - 1975:2	3
		1975:1 - 1975:1	3	1976:1 - 1976:1	3
		1975:3 - 1975:4	6	1977:1 - 1977:3	9
		1976:2 - 1976:4	9	1978:3 - 1978:3	3
		1977:4 - 1978:2	9	1981:4 - 1981:4	3
		1978:4 - 1981:3	24	1983:4 - 1984:1	12
		1982:1 - 1983:3	18	1986:1 - 1987:2	15
		1984:2 - 1985:4	21	1989:4 - 1989:4	3
		1987:3 - 1989:3	27	1993:2 - 1994:1	12
		1990:4 - 1993:1	30	1996:1 - 1996:1	3
		1994:2 - 1995:4	21	1998:1 - 1998:1	3
		1996:2 - 1997:4	21	2000:1 - 2000:1	3
		1998:2 - 1999:4	21	2002:4 - 2002:4	3
		2000:2 - 2002:3	30	2003:3 - 2003:4	6
		2003:1 - 2003:2	6		

### ***3.5 Relationship between Mergers and Acquisitions activity, the Stock Market and the Business Cycle***

A number of earlier studies (Nelson, 1959, Melicher et al., 1983, Geroski, 1984, Clark et al., 1988, Guerard, 1989, Clarke and Ioannidis, 1986) have looked at the relationship between merger activity and the business cycle and/or stock market variables in the USA and UK. Most studies relate to the USA. The majority of the early studies rely on simple correlations between mergers and other variables although a number of more sophisticated studies have appeared in more recent years.

In a classic early study, Nelson (1959) used quarterly data on the USA to consider the relationship between merger activity, stock market prices and industrial production over the period 1895 - 1956. Employing simple regression analysis, he found that there was a positive and significant relationship between merger activity and stock market prices between 1895 and 1920 and, more generally, between 1895 and 1956 whilst he was unable to establish a significant correlation between merger activity and the level of industrial production.

More recent studies have adopted a more sophisticated approach. A good example is the study by Melicher et al. (1983) which analyzed quarterly data on merger activity in the USA in 1947-1977. Using multiple-time-series analysis they found that merger activity was related to both "real" and "capital market" variables in their data. In particular, capital market variables such as stock

prices and bond yields tended to "lead" merger activity whilst mergers tended to "lead" changes in industrial activity and business failures.

Other studies have produced mixed results. Geroski (1984) looked at the relationship between mergers and the stock market index in four data sets. Using Granger causality tests he found no "causal" link between mergers and stock prices in his data. He also found that correlations between his variables were unstable. Clark et al. (1988) found evidence of "Granger causality" (in both directions) between stock prices and mergers in US data in 1919-1971. On the other hand, Guerard (1989) found no evidence of "Granger causality" running from stock prices or industrial production to mergers in US data in 1895-1964.

Clarke and Ioannidis (1996) tested the ability of real stock market prices to "Granger cause" merger activity. They also used two measures of merger activity: the number and the "real" value of mergers. Their results suggest that stock market returns Granger cause mergers. This relationship holds for the UK from January 1971 to April 1993 when stock prices are measured in real terms and when mergers are measured either by number or real value. The evidence is in contrast with the work done by Geroski (1984) who found no evidence of "causality" and significant evidence of instability in his equations. In Clarke and Ioannidis (1996), real stock market returns were found to be stable predictors of both our measures of merger activity.

Until now, most studies have used the number of mergers as the measure of merger activity in their investigations. Also, some of the studies noted above use the nominal value of the stock market index to predict aggregate merger activity." The inclusion of the nominal stock market price in the explanatory set is, in our view, misguided. Fluctuations in the stock market index on their own do not convey any information about the relative valuation of equity vis-a-vis the rest of the goods in the economy. For example, in periods of stagflation, stock market prices may rise but as there are also periods of recession the "real" value of equity may fail. If, therefore, there is an underlying positive relationship between "real" share prices and mergers, the regression of nominal stock market prices and mergers will lead to spurious results (indicating a negative or zero correlation) because of the absence of the effects of the price level in the equation.

In order to examine the relationship between the mergers and acquisitions activity, the stock market and the business cycle a switching regression model<sup>4</sup>, in which the mergers activity is assumed to switch between three regimes, is employed. The three regimes follow the classification identified in the previous section and characterised by periods of "falling", "normal" and "rising" mergers activity respectively. The model takes the following form:

$$y_t = a_0 + a_1 D_1 + a_3 D_3 + \gamma_1 D_1 x_t + \gamma_3 D_3 x_t + \beta_0 x_t + \delta_0 \psi_t + \kappa_1 D_1 \psi_t + \kappa_3 D_3 \psi_t + u_t \quad (3.13)$$

---

<sup>4</sup> A switching regression model has been chosen instead of a Granger Causality approach because the latter lies on the ideas that "cause does not come after effect". This is not in line with the research questions of this thesis. A detailed explanation of switching regression models can be found in Goldfeld and Quandt (1973).

Where,

$x_t$  is the FTSE-ALL SHARES stock market index<sup>5</sup>;

$\psi_t$  is the UK Business Cycle Coincident Index<sup>6</sup>;

$D_1$ ,  $D_3$  are dummy variables.  $D_1$  is equal to one in regime one (i.e. in decreasing mergers activity periods at the end of a merger wave) and equal to zero otherwise. Similarly,  $D_3$  is equal to one in regime three (i.e. in rising mergers activity periods at the beginning of a merger wave), otherwise  $D_3$  equal to zero. The second regime (“normal” merger activity) is captured implicitly by the constant. The use of a third dummy variable would result to perfect collinearity).

If  $\gamma_1$  and  $\gamma_3$  are significantly different from zero the relationship between mergers and acquisitions activity and the Stock Market Index is different under the three different regimes identified in the previous section. In the same path if  $\kappa_1$  and  $\kappa_3$  are significantly different from zero the relationship between mergers and acquisitions activity and the UK Business Cycle Coincident Index is different under the three different regimes. Alternatively, if the estimates of the above coefficient are insignificantly different from zero the relationship between Mergers and Acquisitions activity, the Stock Market and the Business Cycle is the same throughout the three regimes.

Table 3.5 provides estimates for the above equation. Panel A presents regression estimates for the relationship between the mergers and acquisitions

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<sup>5</sup> Downloaded from Datastream

<sup>6</sup> The UK Business Cycle Coincident Index has obtained from the Business Cycle Research Institute and used in this chapter with their permission



activity, the stock market and the business cycle, for the overall period, while panel B provides estimates for the different regimes. All t-statistics presented are corrected for heteroscedasticity and serial correlation.

**Table 3.5: Relationship between Mergers and Acquisitions activity, the Stock Market and the Business Cycle**

<b>Panel A</b>				
Variable	Coefficient	Std. Error	t-Statistic	Prob.
C	-2.963706	1.388729	-2.134114	0.0346
LFTSE	0.798961	0.156814	5.094971	0.0000
LUKCI	2.214213	0.984591	2.248865	0.0261
R-squared	0.166284	Mean dependent var		-0.207987
Adjusted R-squared	0.154023	S.D. dependent var		22.43810
S.E. of regression	20.63789	Akaike info criterion		8.913481
Sum squared resid	57925.46	Schwarz criterion		8.976815
Log likelihood	-616.4869	F-statistic		13.56252
Durbin-Watson stat	2.730380	Prob(F-statistic)		0.000004

<b>Panel B</b>				
Variable	Coefficient	Std. Error	t-Statistic	Prob.
C	-5.918608	1.387508	-4.265639	0.0000
D1	-18.34786	10.46860	-1.752657	0.0820
D3	18.33162	4.492891	4.080139	0.0001
LUKCI	2.211499	1.189388	1.859359	0.0652
D1UKCI	-3.398960	5.263910	-0.645710	0.5196
D3UKCI	-1.837340	2.255591	-0.814571	0.4168
LFTSE	0.566539	0.175559	3.227067	0.0016
D1FTSE	-0.164831	0.573277	-0.287524	0.7742
D3FTSE	0.009531	0.300361	0.031731	0.9747
R-squared	0.304237	Mean dependent var		-0.207987
Adjusted R-squared	0.261421	S.D. dependent var		22.43810
S.E. of regression	19.28345	Akaike info criterion		8.818928
Sum squared resid	48340.68	Schwarz criterion		9.008930
Log likelihood	-603.9155	F-statistic		7.105645
Durbin-Watson stat	2.904025	Prob(F-statistic)		0.000000

The results in Panel A provide consistent evidence for the relationship between Mergers and Acquisitions activity, the Stock Market and the Business Cycle. For the overall period (1969:1 through 2003:4) the relationship is reliably positive. However, coefficients (panel B) are insignificantly different from zero at 95% level of significance, so the relationship between the mergers and

acquisitions activity, the stock market and the business cycle is of the same nature under the three different regimes of mergers and acquisitions activity.

### ***3.6 Summary and Conclusions***

The objective of this chapter is to provide quantitative evidence on the merger wave hypothesis. Using a model of Markovian parameter switching and recent merger data for the UK, merger waves were identified and dated. The interpretation of mergers activity as a mean and variance switching autoregressive process provides a useful quantitative operationalization of the wave hypothesis.

More specifically, the empirical evidence suggests that there exist three distinctly different types of behaviour (regimes) in the series of mergers and acquisitions numbers. The results reported here suggest that the majority of the time the series is relatively stable (regime 2), but also that periods of dramatic fall (regime 1) or sharp rise (regime 3) can also be identified. Whenever one of these other periods occurs, the data is more likely to flatten out, if only for a short time, before changing direction. Thus, the dominance of Regime 2 is not a surprising result, nor is the fact that this regime has the longest expected duration. More surprising, however, is the longer duration associated with Regime 1 as compared to Regime 3, suggesting that the start of a merger wave is often marked by an explosive increase in takeover activity, which is considerably steeper than the drop marking the end of the wave. This offers an

explanation for the failure of previous attempts to model merger waves as bubbles.

At a second stage the contemporaneous relationship between the Mergers and Acquisitions activity in the UK with the Stock Market and the aggregate economic activity (Business Cycle), is found to be significant. However, when the relationship between the mergers and acquisitions activity, the stock market and the business cycle is examined under each one of the regimes of mergers and acquisitions activity, the evidence suggests that the relationship remains in all the three regimes.

## **Chapter 4: The Market for Corporate Control, the Macroeconomic Activity and the Stock Market: A Sectoral Study.**

### ***4.1 Introduction***

The wave behaviour of mergers and acquisitions has puzzled researchers for a long period (e.g. Moody, 1904, Bain, 1944, Stigler, 1950, Nelson, 1959, and Scherer and Ross, 1990). There have been considerable attempts to further explain particular episodes of mergers and acquisitions waves. However, the lack of a unified theoretical framework, lead researchers to more general explanatory empirical studies that aimed at characterising the data generation process underlying the mergers and acquisitions activity. More specifically, they focused on descriptive assessments of mergers and acquisitions time series either by means of linear models as in Melicher et al. (1983), Shugart and Tollinson (1984) and Clark et al. (1988), or by employing simple limited tests for detecting wave behaviour as in Golbe and White (1987, 1993).

In the following years, the empirical literature in the area consists mainly by studies that have implemented non-linear models in an attempt to capture and better describe abrupt shifts in mergers and acquisitions behaviour. In fact, Markov Switching models were considered by Town (1992), Linn and Zhu (1997) and Resende (1999) for aggregate mergers and acquisitions activity in the U.S.A and

the U.K.<sup>1</sup>. Some stylized facts appear to be slowly emerging. First, Markov Switching models seem to provide a better portrayal of mergers and acquisitions than simpler formulations involving, for instance the random walk hypothesis. Second, there is empirical evidence of a high degree of persistence of the unobserved states for mergers and acquisitions activity. At this stage, it is important to stress out that the trajectory of the time series literature on mergers and acquisitions displayed a similar evolution as the empirical literature in the area of exchange rates as indicated by Meese and Rogoff (1983) and Engel and Hamilton (1990).

This chapter is designed to analyze the behavior of the corporate control market in the UK during a period that incorporates excessive acquisitions activity in this country, at a sectoral level. In other words it applies the insights into aggregate merger process gained in the previous chapter to the industry level. This will enable us to further develop our understanding of aggregate merger and acquisition activity, and to provide answers to questions regarding their behavior at sectoral level, thus completing the description of the dynamic behavior of aggregate merger and acquisition activity.

This is motivated by the fact that different aggregate measures examined so far, by the relevant empirical literature, are necessarily aggregations of processes at the sector level. Thus it is quite possible the set of aggregate determinants of merger

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<sup>1</sup> For a more detailed discussion of the literature please refer to the relevant section of the second chapter of this thesis (3.2.2).

and acquisition activity described in the previous chapter, to be in fact a combination of industry specific determinants.

Evidence for difference among industries with respect to the intensity of merger and acquisition activity, indicative of an industry driven aggregate merger process has been quoted in the literature for almost half a century (Nelson, 1959); where the probability of industry level drivers seems to becoming a common belief among researchers and practitioners. Over the last fifty years, a considerable number of researchers attempted to provide micro- or macro explanations for this (e.g. Gort, 1969, McGowan, 1971, Salant et al., 1983, Deneckere and Davinson, 1985, Pery and Porter, 1985, Blair and Schary. 1993, and Bittlingmayer, 1996). On the other hand side, others used the “industry life cycle” concept to explain this in the presence of different types of merger and acquisition activity at different stages of an industry’s development (e.g. Dutz, 1989, and Weston et al., 1990).

Apart from the above described attempts to explain the inter-industry variations of merger activity, more recently, a strand in the literature has emerged to document the occurrence and describe the effects of takeovers on different sectors of the economy. This includes, among others, the role of horizontal mergers in the declining USA steel industry (Hogan, 1984) and the USA railroads (Fischer and Lande, 1983),, mergers as a way of gaining market power in the USA airline industry (Kim and Singal, 1993), the advertising industry (Jung and Sheldon, 1995), and the UK oil industry (Driffield, 1999). Moreover, there are studies they

approach mergers and acquisitions as a response to technological shocks (e.g. Weston, Johnson and Siu, 1999 in the chemical industry).

More closely related to this chapter, Mitchell and Mulherin (1996) investigate the possibility of distinct industrial merger waves. According to their empirical findings the USA aggregate mergers and acquisitions activity is the result of industry wide phenomena triggered by economic shocks at a sectoral level, consistent with the suggestion of industry driven merger and acquisition waves. However, they also acknowledge that inter-industry variations in takeover activity may entail an adaptation of industry structure to a changing economy, thus leaving open the possibility of macro-determinants of takeovers.

More recently, Resende (1999) investigates the behavior of mergers and acquisitions in the UK at the sectoral level, allowing the serie to be developed in two regimes, rejecting the random walk specification.

More specifically, this chapter has three main objectives in studying further the characteristics of the aggregate mergers in the UK. First, it aims to determine formally the presence of mergers waves in different industrial sectors making use of the Markov switching models with no autoregressive dynamics and constant transition probabilities along the lines of Hamilton (1990) and applied by Engel and Hamilton (1990) in the context of exchange rates. These models have the capacity to capture abrupt changes in the evolution of a given time series. It

extends existing research by using a Markov Switching Model, allowing the series to follow three regimes with different mean values enabling the series to be modeled using multiple time series representations. The three regimes defined here represent the series (1) in decreasing mergers activity periods at the end of a merger wave, (2) in normal mergers activity period, and (3) in rising mergers activity period at the beginning of a merger wave. Examining each of these different types of behavior provides a considerably more informative picture of the behavior of the series over time than has been previously available. The dataset employed covers mergers activity in the UK from 1969:1 through 2003:4.

Second, it attempts to examine the relationship the Mergers and Acquisitions activity in the UK with the Stock Market and the aggregate economic activity (Business Cycle), at a sectoral level. Finally, it is reasonable to consider that the relationship between the Mergers and Acquisitions activity, the Stock Market and the Business cycle might be significantly different during periods of falling, rising or stable Mergers activity for each one of the industrial sectors under consideration.

The remaining of the chapter is organized as follows. The second section the data used in this chapter. The third section presents the empirical results. The fourth section discusses the relationship between Mergers and Acquisitions activity in the UK with the Stock Market and the aggregate economic activity (Business Cycle), for each one of the industrial sectors. Finally, the fifth section contains some concluding remarks.



## ***4.2 Data Description***

A major difficulty in time series analysis of mergers and acquisitions is the necessity of relatively long series. In the recent past, empirical studies for the USA have merged series produced by different institutions, but such a procedure is quite problematic. This chapter investigates mergers and acquisitions in the UK, at a sectoral level, for which the longest consistent series available is considered. More specifically, total numbers of mergers and acquisitions of independent companies are considered. The present chapter makes use of quarterly data at sectoral level. Sector classification changes limit our sample period from 1985 (1<sup>st</sup> quarter) to 2005 (4<sup>th</sup> quarter). In addition, industrial sectors, where mergers and acquisitions were virtually non-existent such as the tobacco industry, were disregarded. The basic data source was the Securities Data Corporation (SDC) merger and acquisition database<sup>2</sup>. The industrial sectors considered are: Consumer Products and Services, Financial Companies, Healthcare, Industrials, Basic Materials, Media and Entertainment, Retail, High Technology, Telecommunications and Oil and Gas. Table 4.2.1 presents summary statistics for the quarterly data described above.

Even the most superficial examination of the series of acquisition numbers is sufficient to reveal that most of them are clearly not series that behave in a conventional manner, as Figure 4.2.1 (a-j) demonstrates. The majority of the series

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<sup>2</sup> Prior to 1985, there is few data available from the Securities Data Corporation (SDC) database for UK mergers and acquisitions.

are characterized by stable periods, typified by relatively small changes between observations. In addition to the stable regime, there are also periods of explosive growth and dramatic falls that denote the beginning and end of the merger waves and these also need to be taken into consideration.

The data is  $I(1)$ <sup>3</sup>, with the exception of Healthcare and Oil<sup>4</sup> and Gas industrial series that are stationary. Figure 4.2.2 (a-j) represents the data after making it stationary.

The remaining data for the UK, used in this chapter, had the following sources:

- a. The UK Business Cycle Coincident Index (UKCI) has obtained from the Economic Cycle Research Institute.
- b. The FTSE ALL SHARES industrial indices have been downloaded from Datastream International database.

At this point we need to note that industrial sector classification used in this chapter follows the new FTSE Industry Classification Benchmark (ICB)<sup>5</sup>.

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<sup>3</sup> Augmented Dickey – Fuller (ADF) Test for stationarity generated probabilities of 0.2446 for Consumer Products, 0.1081 for Financial, 0.0882 for industrials, 0.0518 for Materials, 0.052 for Media, 0.1080 for Retail, 0.0519 for technology and 0.0504 for Telecommunications industrial sectors, all higher than 0.05, so the null hypothesis of a Unit Root is not rejected at 5% level of significance.

<sup>4</sup> ADF Test generated probabilities of 0.0192 and 0.0218 for Oil & Gas and Healthcare industrial sectors respectively, both less than 0.05, so the null hypothesis of a Unit Root is rejected at 5% level of significance.

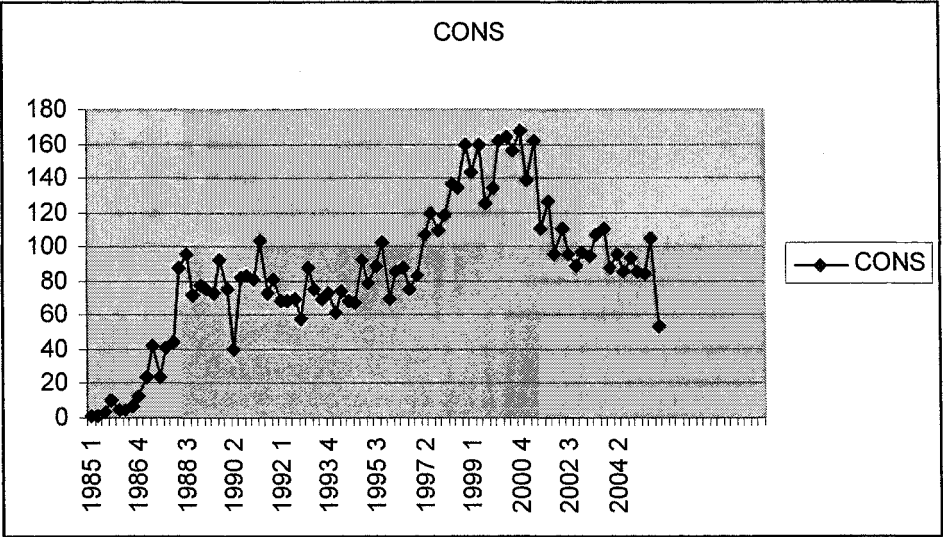
<sup>5</sup> For more information on the structure of each industrial sector please see the Appendix.

Table 4.2.1: Summary statistics for the quarterly mergers and acquisitions data (1985/1 to 2005/5).

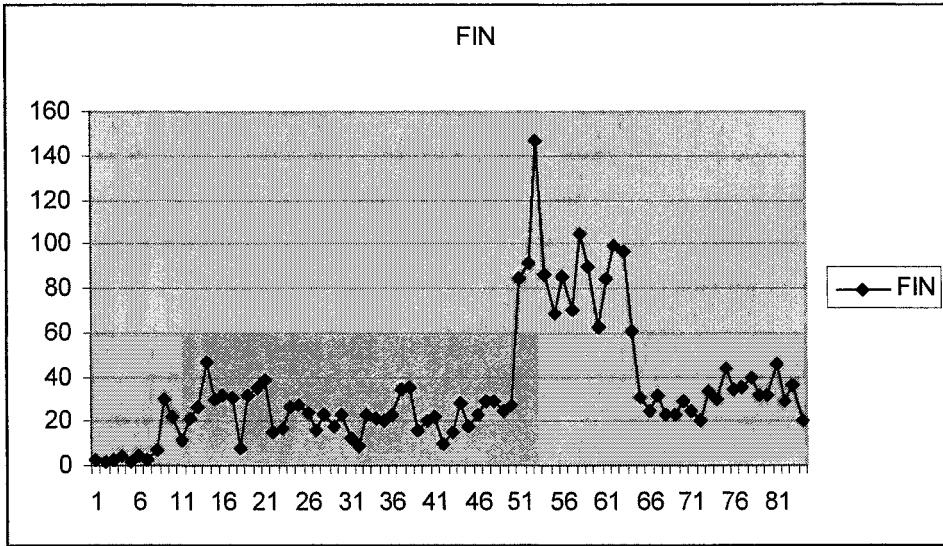
	CONS	FIN	HEA	IND	MAT	MED	RET	TECH	TEL	OIL
Mean	4.806005	1.245872	1.939082	2.542426	1.474428	2.69965	3.135771	3.043047	2.578393	3.547517
Standard Error	3.518754	2.851838	5.278199	3.025426	3.504036	3.820875	2.812367	4.424568	5.385535	6.911729
Median	2.898754	0	0	0.803217	-2.66682	-3.0153	3.571808	0	0	0
Mode	0	-28.7682	0	69.31472	-22.3144	-2.92704	0	0	0	0
Standard Deviation	32.05738	25.98148	48.08668	27.56294	31.92329	34.80983	25.62188	40.30973	49.06456	62.96884
Sample Variance	1027.675	675.0372	2312.329	759.7157	1019.096	1211.724	656.4807	1624.875	2407.331	3965.075
Kurtosis	2.834689	0.958646	2.433053	1.721492	2.905586	2.368935	0.065874	2.768387	2.041936	2.349828
Skewness	0.848327	0.277356	0.26481	0.075932	0.665747	0.719216	0.134105	0.469712	0.556078	-0.10866
Range	189.712	142.5515	317.8054	165.3609	211.8662	230.2585	125.2763	259.8566	317.8054	402.5352
Minimum	-69.3147	-69.3147	-138.629	-84.2679	-95.5511	-91.6291	-55.9616	-129.928	-138.629	-207.944
Maximum	120.3973	73.23679	179.1759	81.09302	116.3151	138.6294	69.31472	129.9283	179.1759	194.591
Sum	398.8984	103.4074	160.9438	211.0213	122.3775	224.071	260.269	252.5729	214.0066	294.4439
Count	83	83	83	83	83	83	83	83	83	83

Figure 4.2.1: Mergers and Acquisitions in the UK: Industrial Sectors

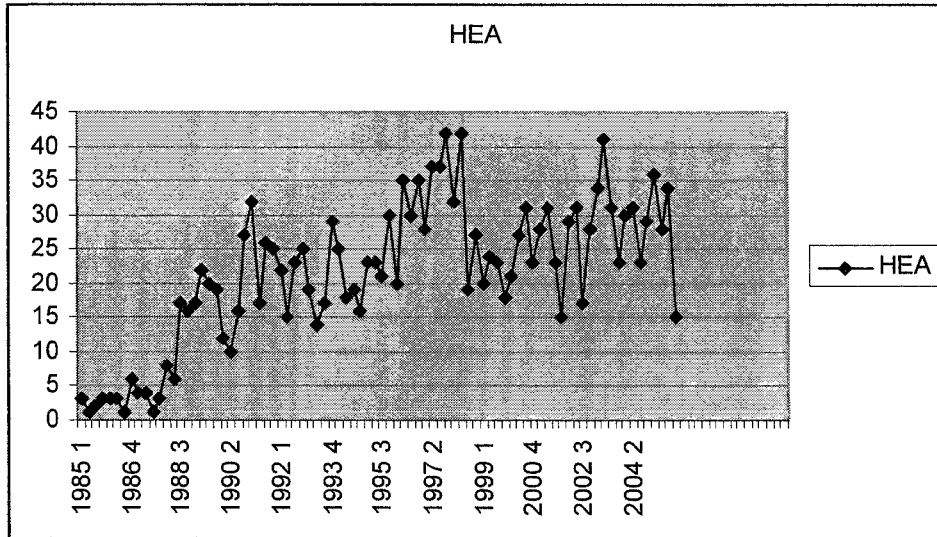
(a) Consumer Products and Services



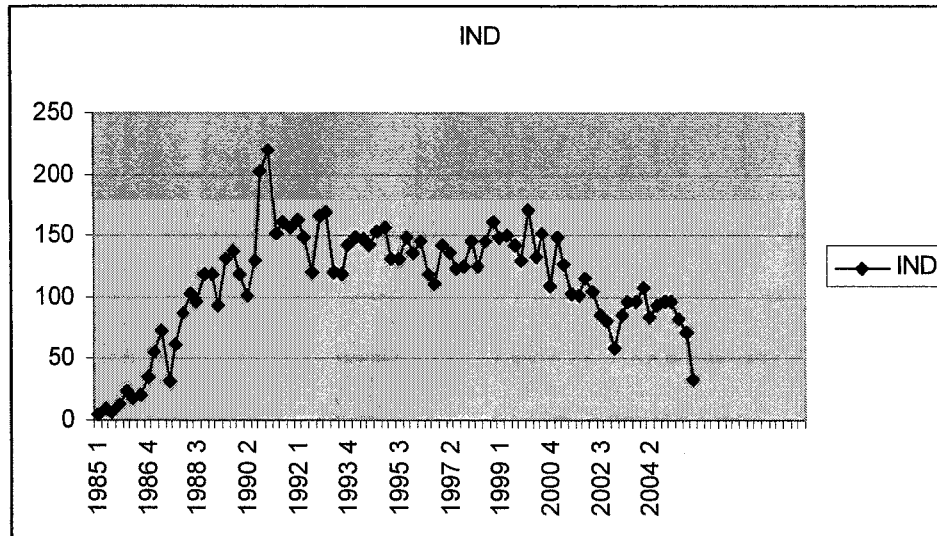
(b) Financials



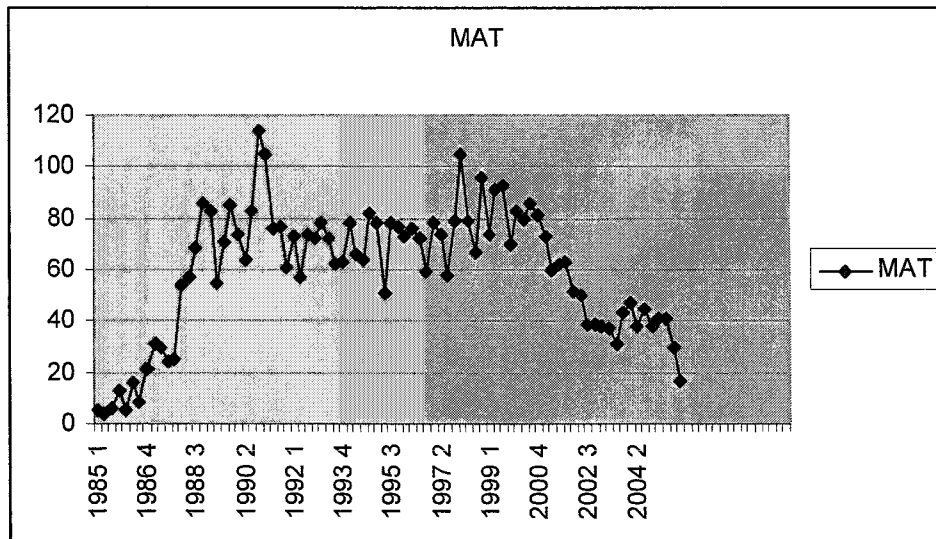
(c) Healthcare



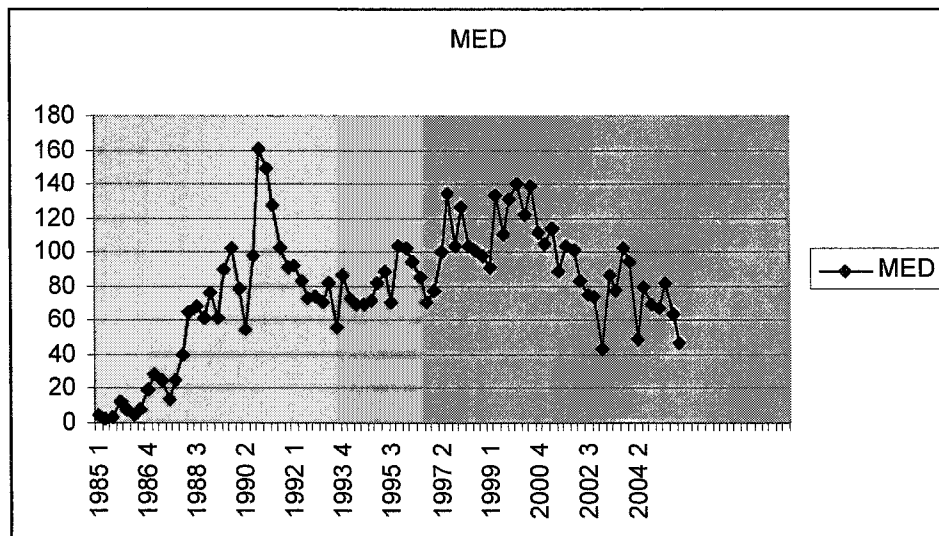
(d) Industrials



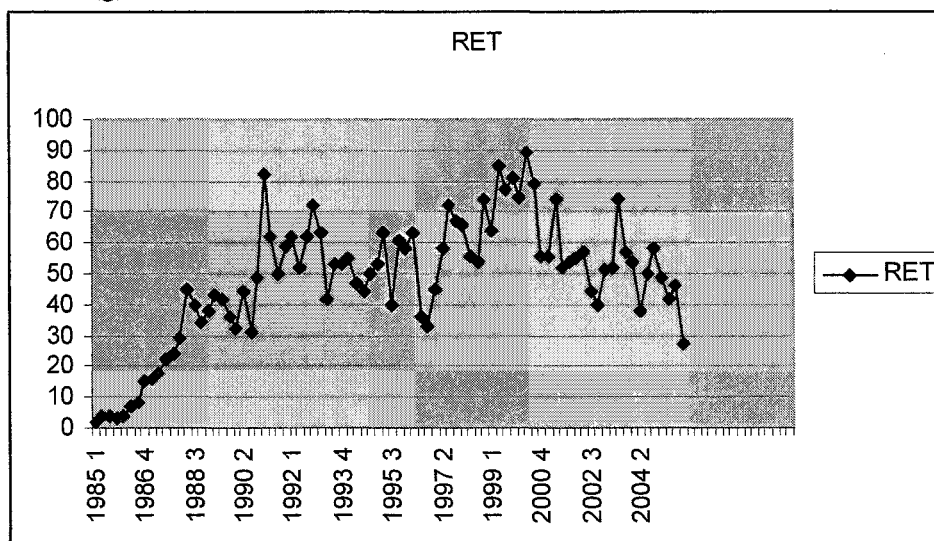
(e) Materials



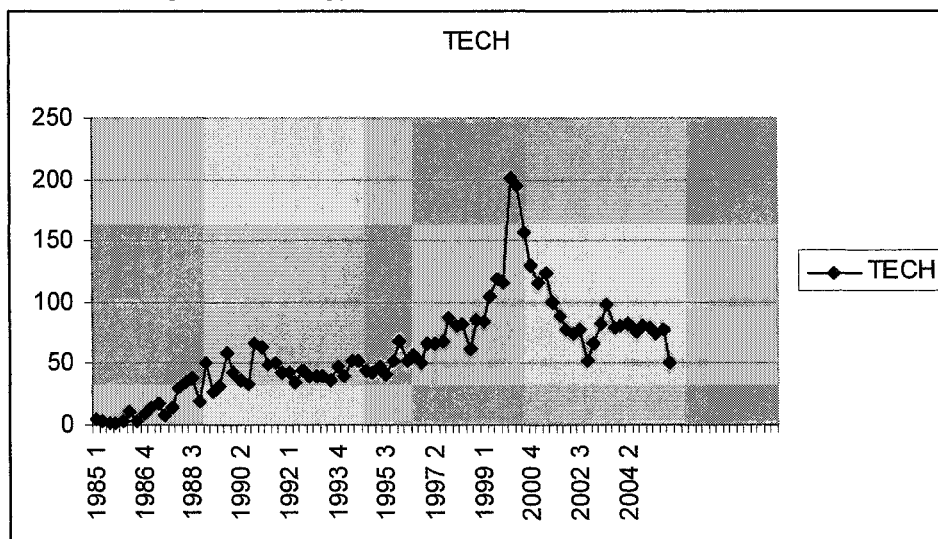
(f) Media and Entertainment



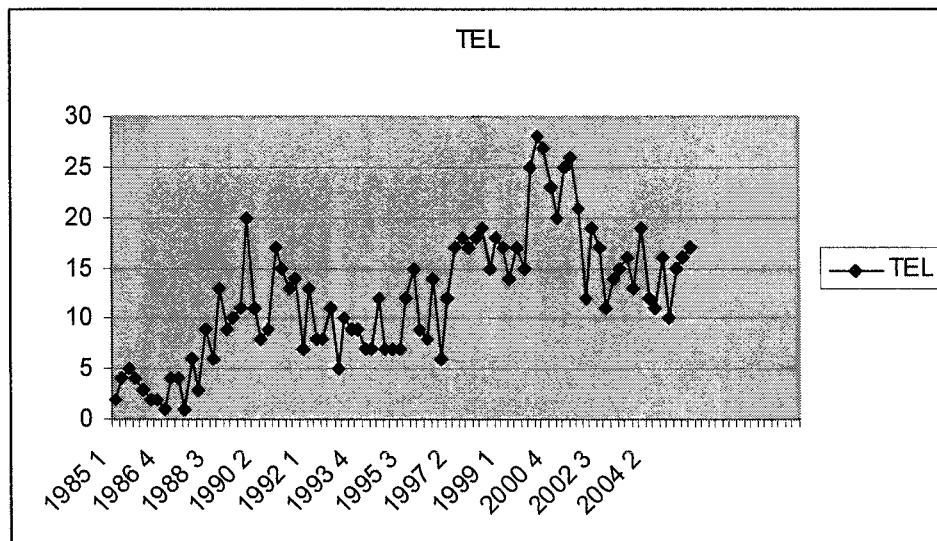
(g) Retail



(h) High Technology



(i) Telecommunications



(j) Oil and Gas

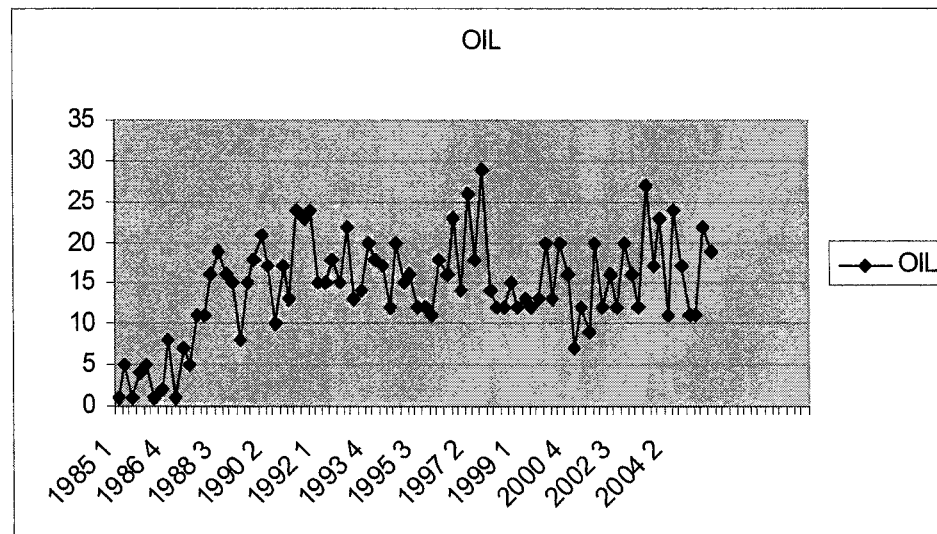
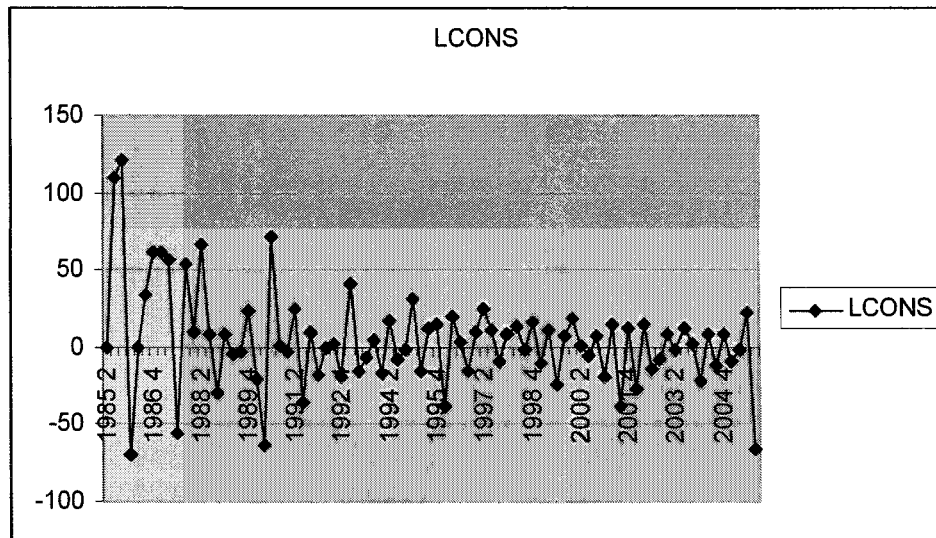


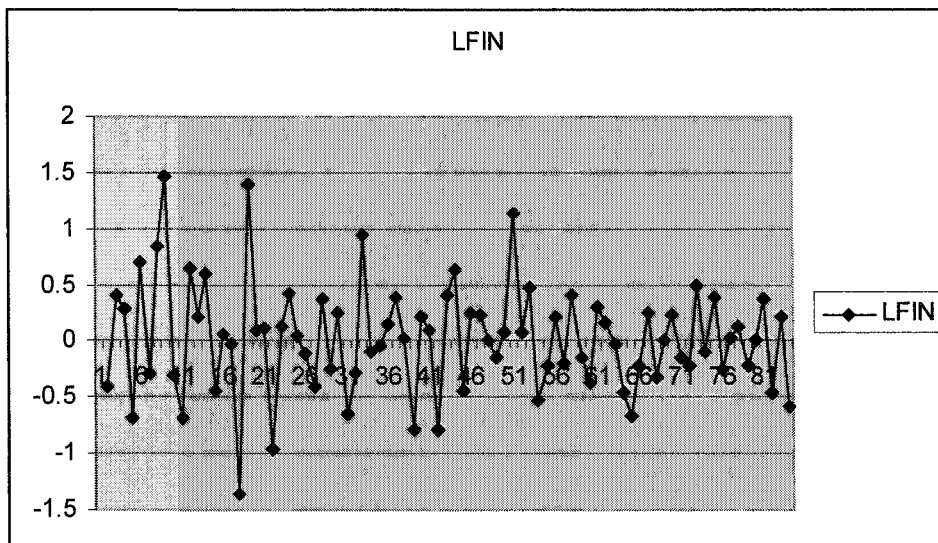


Figure 4.2.2: Mergers and Acquisitions in the UK: Industrial Sectors

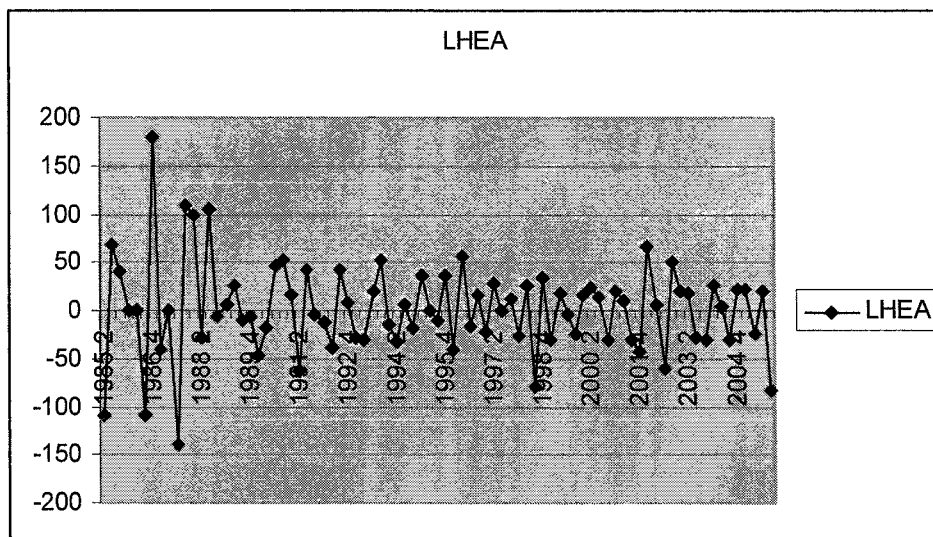
(a) Consumer Products and Services



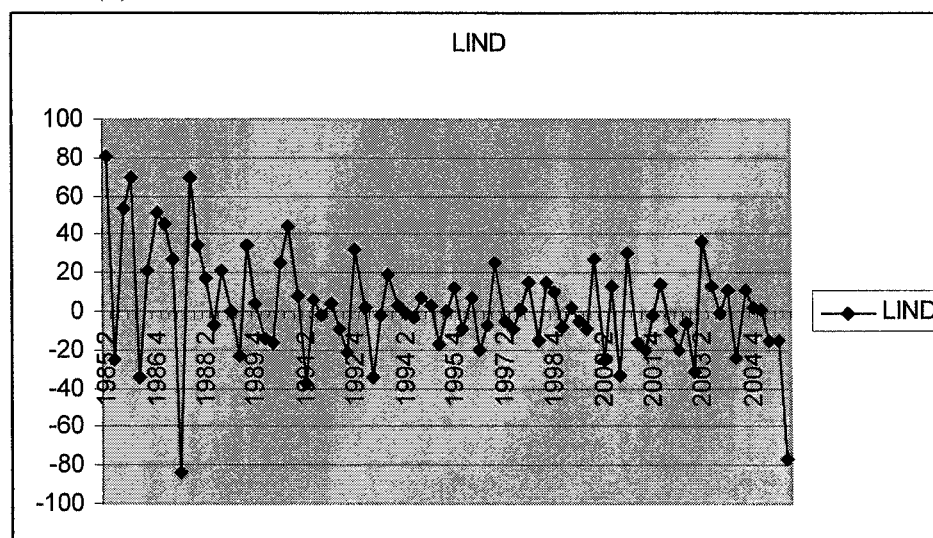
(b) Financials



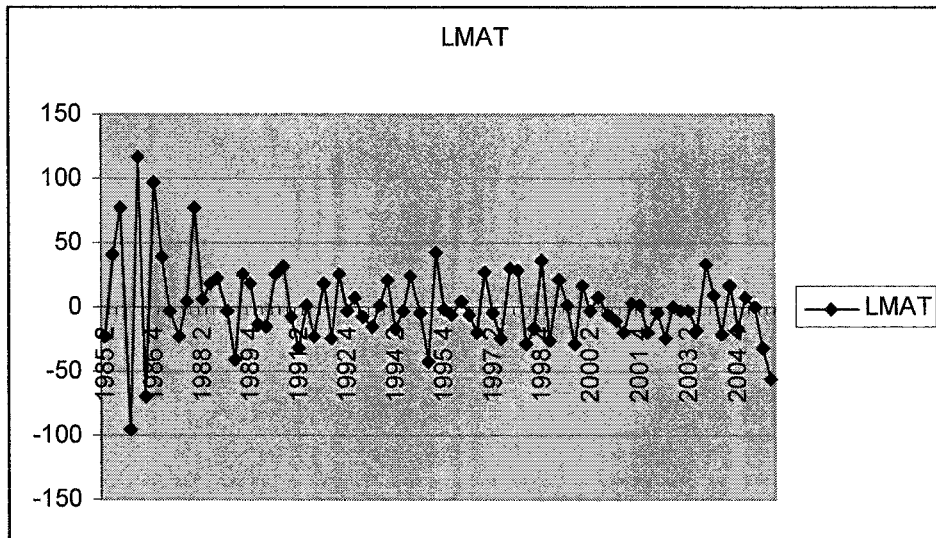
(c) Healthcare



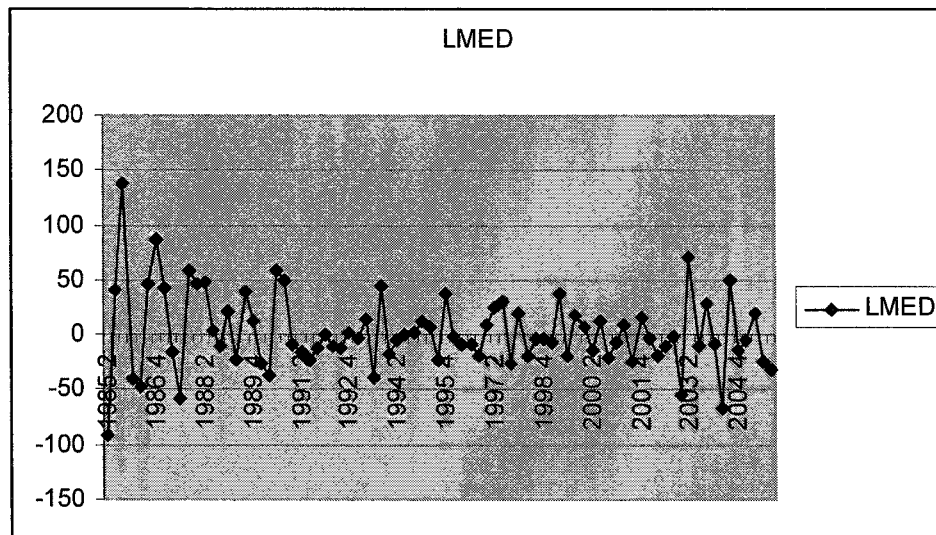
(d) Industrials



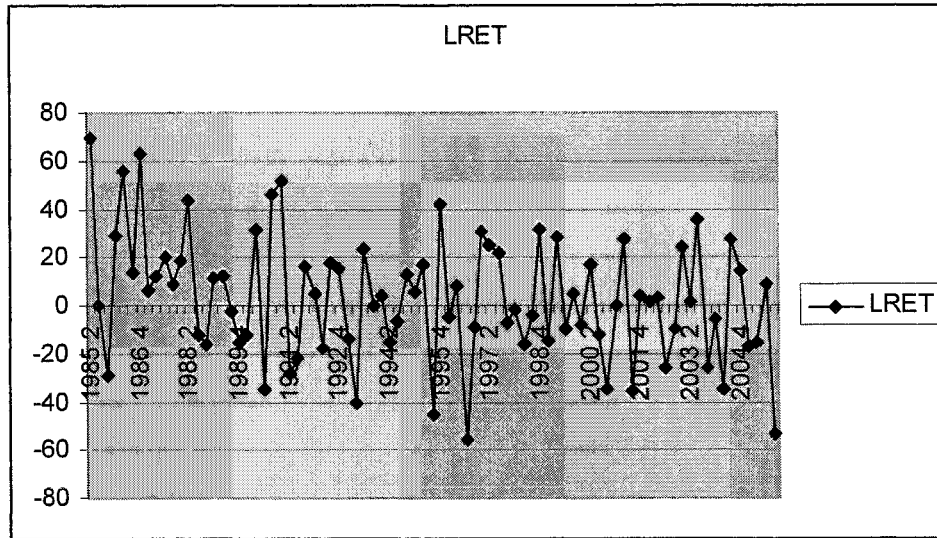
(e) Materials



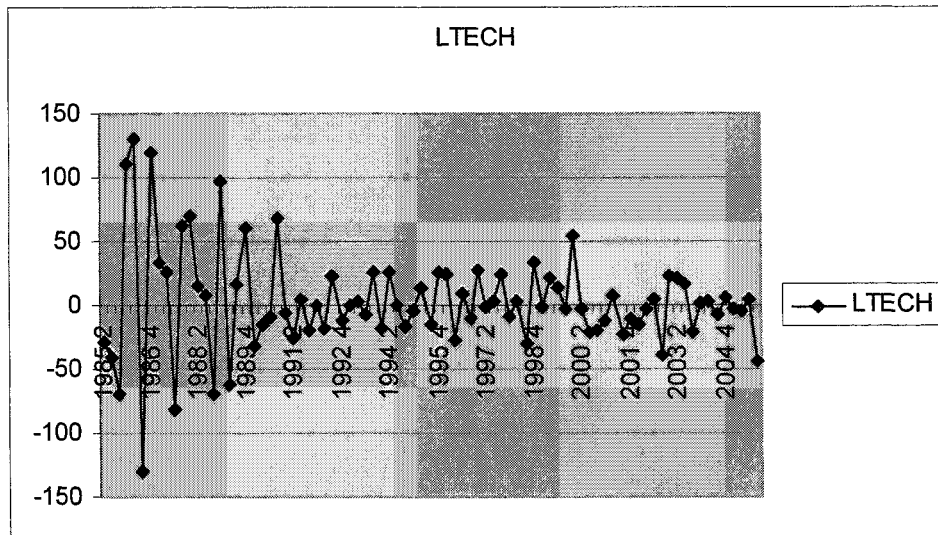
(f) Media and Entertainment



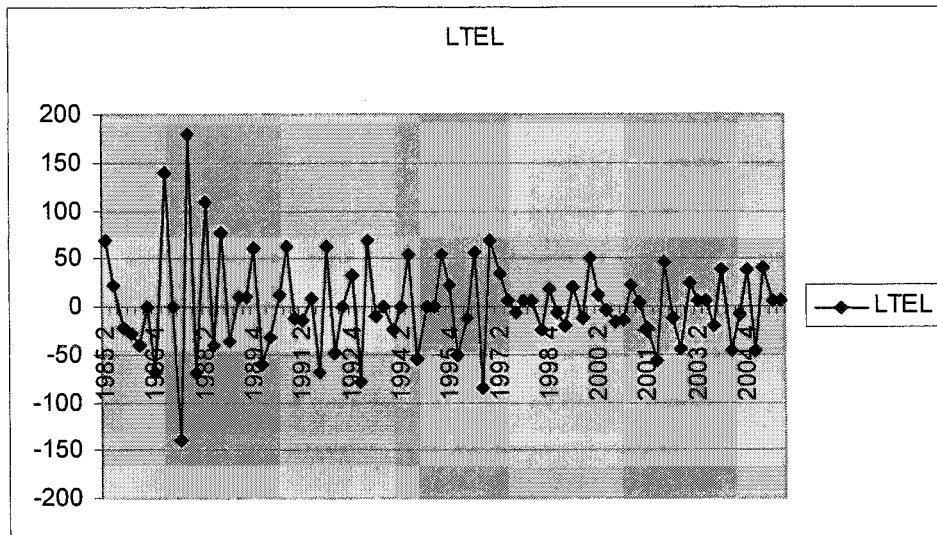
(g) Retail



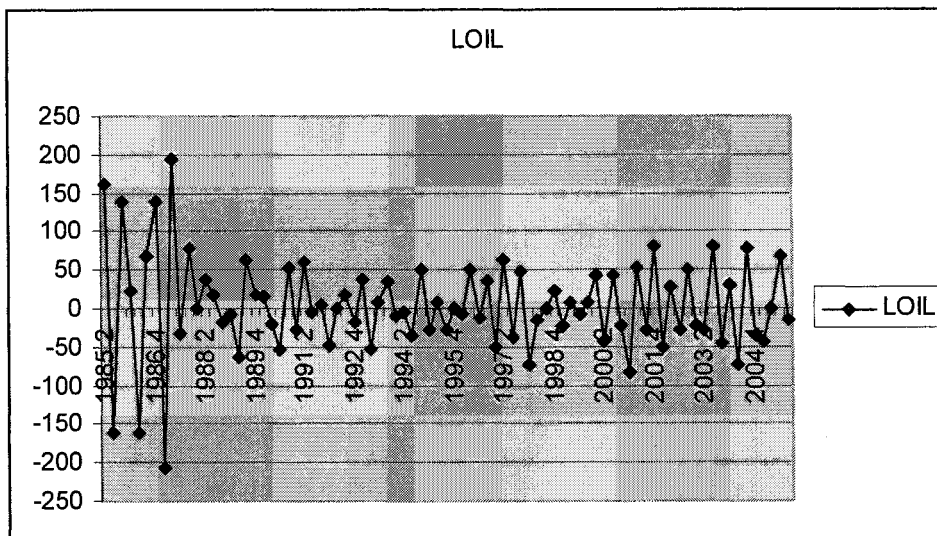
(h) High Technology



(i) Telecommunications



(j) Oil and Gas



### 4.3 Empirical Results

Using the Markov Switching model over three regimes, this data will be modeled as an autoregressive process of order 4, across the lines of chapter 3, and typified by equation 3.10.

The transition matrix will be of the form given by equation 3.11.

Across the lines of Chapter three the empirical results reported here are all generated using Ox version 3.2<sup>6</sup> (Doornik, 2002) and MSVAR<sup>7</sup> version 1.31e (Krolzig, 2003). The results support the hypothesis that there are three distinct regimes in the series of a number of industrial sectors. A likelihood ratio (LR) test rejects the possibility of fitting a linear model to the series and this result remains true when the test is adjusted in the manner advocated by Davies (1977, 1987). The test proposed by Davies is a modified form of the LR test which gives a corrected

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<sup>6</sup> **Ox** is an object-oriented statistical system. At its core is a powerful matrix language, which is complemented by a comprehensive statistical library. Among the special features of Ox are its speed, well-designed syntax and editor, and graphical facilities. Ox can read and write many data formats, including spreadsheets and OxMetrics files; Ox can run most econometric Gauss programs.

<sup>7</sup> **MSVAR** is an Ox package designed for the econometric modeling of univariate and multiple time series subject to shifts in regime. It provides the statistical tools for the maximum likelihood estimation (EM algorithm) and model evaluation of *Markov-Switching Vector Autoregressions* as discussed in Krolzig (1997).

A variety of model specifications regarding the number of regimes, regime-dependence versus invariance of parameters etc. provides the necessary flexibility for empirical research and will be of use to econometricians intending to construct and use models of dynamic, non-linear, non-stationary or cointegrated systems.

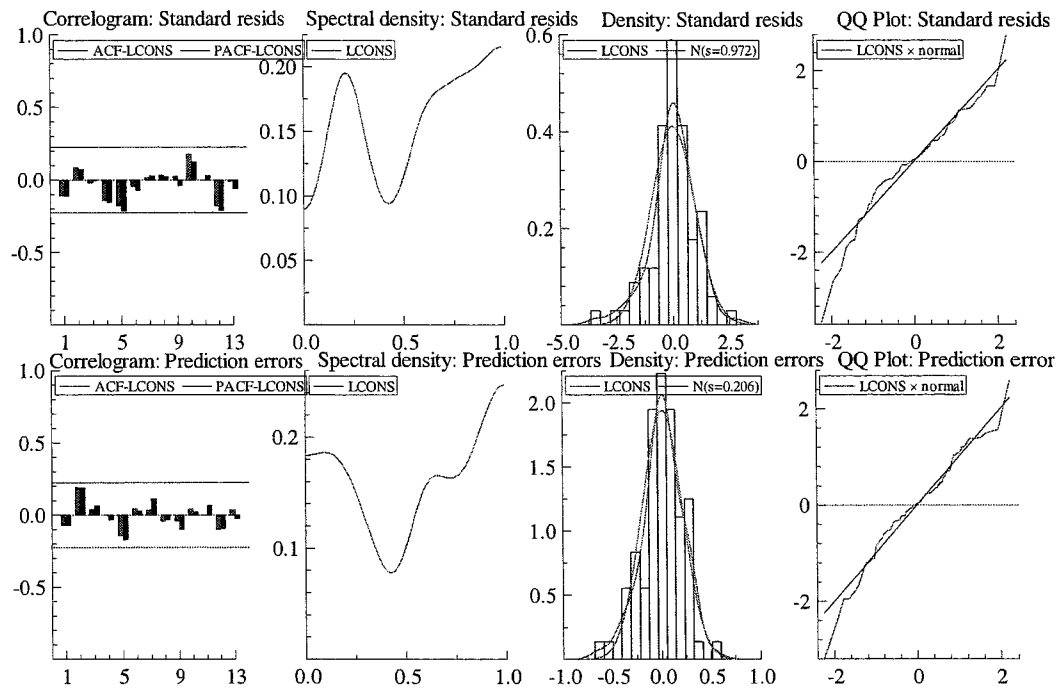
**MSVAR** can be used by writing a small Ox program. Ox is an object-oriented matrix language with a comprehensive mathematical and statistical function library. As **MSVAR** derives from the Modelbase class, it allows the easy use and exchange with other classes such as PcFiml. In conjunction with Ox Professional, **MSVAR** can be used interactively via the user-friendly interface OxPack in combination with GiveWin 2 for data input and graphical and text output.

upper bound for the probability value. (For a clear and concise description of the test devised by Davies (see Garcia and Perron, 1996). In the following subsection the empirical results generated for each one of the industrial sectors will be discussed, together with the models robustness.

#### ***4.3.1 Mergers and Acquisitions Waves in Consumer Goods Industrial Sector.***

The model diagnostics are illustrated in Figure 4.3.1.1 and they suggest that the model is generally well-specified. The density and QQ plots both suggest that the model is well-specified, as they are very close to normal distributions for both the standardized residuals and the predictive errors.

**Figure 4.3.1.1: Model Diagnostics for Consumer Goods Industrial Sector**



The estimated coefficients for this model are given in Table 4.3.1.1.

**Table 4.3.1.1: Estimated Parameters from the Three Regimes for Consumer Goods Industrial Sector**

Regime Dependent Mean Values	
$v_1$	-0.0192 (-1.3239) ***
$v_2$	-0.0308 (-1.4200) ***
$v_3$	-0.3124 (8.2298) ***
Autoregressive Coefficients $\theta_{im}$	
$\Delta y_{t-1}$	-0.6777 (-6.4571) ***
$\Delta y_{t-2}$	-0.5112 (-5.2483) ***
$\Delta y_{t-3}$	-0.3804 (-4.6077) ***



$\Delta y_{t-4}$  $-0.3720 (-4.6195)^{***}$ 

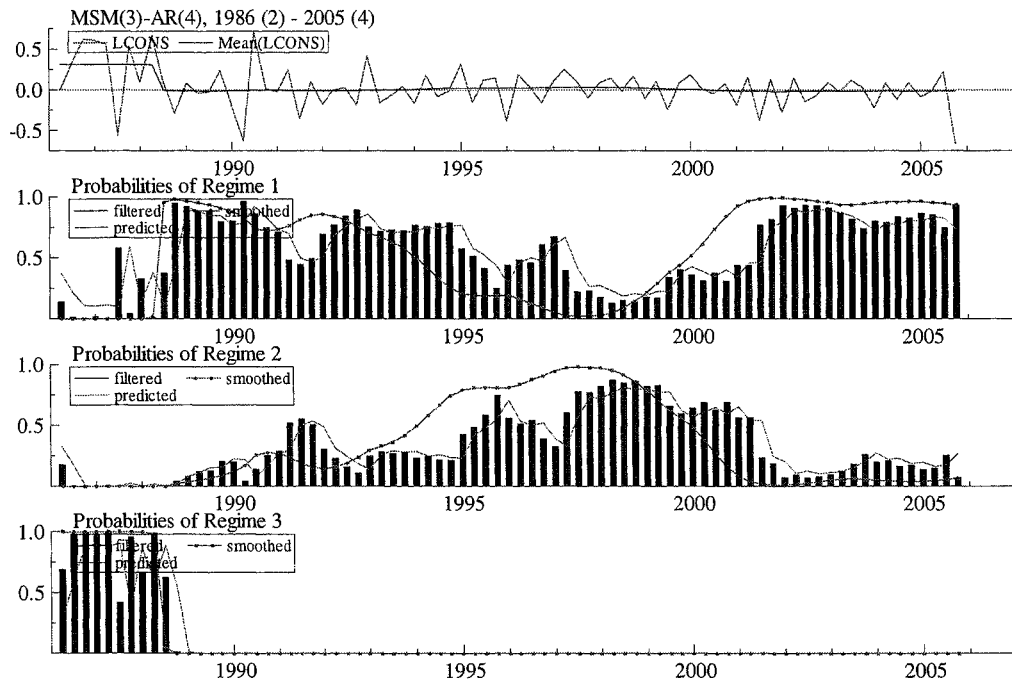
\*\*\*, \*\*, \* Denotes significance at 1%, 5% and 10% respectively

The mean values are clearly different, supporting the hypothesis that the series follows three distinct regimes over the sample period and the coefficients on the four lags are all statistically significant. The transition matrix for these regimes is given in table 4.3.1.2 and the regime probabilities are illustrated in 4.3.1.2.

**Table 4.3.1.2: Transition Probabilities for Consumer Goods Industrial Sector**

	<b>Regime 1</b>	<b>Regime 2</b>	<b>Regime 3</b>
<b>Regime 1</b>	0.9566	0.04339	2.308e-008
<b>Regime 2</b>	0.07127	0.9287	4.648e-009
<b>Regime 3</b>	0.09974	2.795e-012	0.9003

**Figure 4.3.1.2: Regime Probabilities for Consumer Goods Industrial Sector**



In these results, Regime 1 represents the periods in which the series is dropping sharply at the end of a merger wave, Regime 2 represents the more stable periods in between the increases and decreases and, finally, Regime 3 represents the periods in which the series is rising rapidly as a merger wave develops.

The dominant regime is clearly Regime 1, which could be described as the decreasing period of mergers and acquisitions activity. When the series is in Regime 1 it is most likely to remain in that regime (95.66%), while the probability of the series flattening out and moving to Regime 2 is quite low (4.339%). There is virtually no chance of the series changing directly from Regime 1 to Regime 3.

The probability that the series will remain in Regime 2, given that it is currently there, is extremely high (92.87%). If the series deviates from Regime 2, it is more likely to move to Regime 1 (7.127%), than Regime 3, but neither of these changes has a particularly high probability. Finally, when the series is rising (Regime 3), it is most likely to remain in the same regime (90.03%). If the data does not remain to Regime 3, it is most probable that it will move to Regime 1 (9.974%). The probability of a change to Regime 2 is practically non existent.

In addition to the transition probabilities, the expected duration for each of these regimes can also be calculated and appears in Table 4.3.1.3.

**Table 4.3.1.3: Durations of the Three Regimes for Consumer Goods Industrial Sector**

	<i>Number of Observations</i>	<i>Ergodic Probability</i>	<i>Duration</i>
Regime 1	44.4	0.6216	23.05
Regime 2	25.6	0.387	14.03
Regime 3	9.0	0.000	10.03

The durations confirm the information supplied by the transition probabilities. The expected duration of Regime 1 is considerably longer than the durations of either of the other two regimes, and the majority of the data demonstrates this decreasing behavior. When considering Regimes 2 and 3, it is clear that more stable periods tend to last longer than increases, as indicated by the longer expected duration for Regime 2.

Following work on business cycle asymmetry by Clements and Krolzig (2003), tests are conducted to determine whether the increases and decreases in the series of merger waves are symmetric or not. The first test is for “sharpness”, or asymmetry, in the peaks and troughs of the data. This test evaluates whether the peaks and troughs are similar in nature, or if one is more rounded and the other sharper. The null hypothesis in this test is that there is no difference in the turning points and this is tested by determining whether the transition probabilities to and from the outer regimes are the same. For the three regime model estimated here, accepting the null hypothesis jointly requires  $p_{13}=p_{31}$ ,  $p_{12}=p_{32}$  and  $p_{21}=p_{23}$ . Given the nature of the merger and acquisition data, it is unlikely that the null hypothesis will be rejected in this test.

The second test is for “deepness” which determines whether the amplitude of the troughs is substantially different to the amplitude of the peaks and, as before, the null hypothesis is that there is no difference. This is a form of Wald test and is based on an evaluation of the skewness of the data. Once again, given the fact that merger waves appear to represent a temporary deviation in the series away from its normal value, it is reasonable to expect that this null hypothesis will also be accepted.

Finally, there is the test for “steepness” which investigates the possibility that the movement of the series in one direction is significantly steeper than in the other direction. This is the most pertinent of these tests in relation to the merger and

acquisition data. The null hypothesis is that there is no difference in the steepness but, following the analysis of the regime durations, it is expected that this hypothesis will be rejected for this data.

The results for these three tests reported in Table 4.3.1.4 and match our expectations. There is no evidence of differences in the sharpness or deepness of the periods in which the merger waves start and fall but there is evidence of significant differences in the steepness with which the waves begin and end. The null hypothesis of no difference in steepness is rejected at the 5% level, which supports the earlier supposition that merger waves begin more rapidly than they end.

**Table 4.3.1.4: Tests of Asymmetry for Consumer Goods Industrial Sector**

<i>Test</i>	<i>Calculated Value</i>
<b>Sharpness Test</b>	11.8872
<b>Deepness Test</b>	1.1815
<b>Steepness Test</b>	3.4804**
***, **, * Denotes significance at 1%, 5% and 10% respectively	

The next step is to identify the specific dates for regimes 1, 2 and 3. In Markov-switching models, the classification and the dating of the regimes amounts to assigning every observation  $y_t$  to a given regime  $m=1,...,M$ . The rule that is applied here is to assign the observation at time  $t$  according to the highest smoothed probability, i. e.:

$$m^* = \arg \max_m Pr(s_t = m | Y_T)$$

At every point in time, a smoothed probability of being in a given regime is calculated (the inference is made using the whole set of data points), and this observation will be assigned to a given regime according to the highest smoothed probability. The following table presents the results.

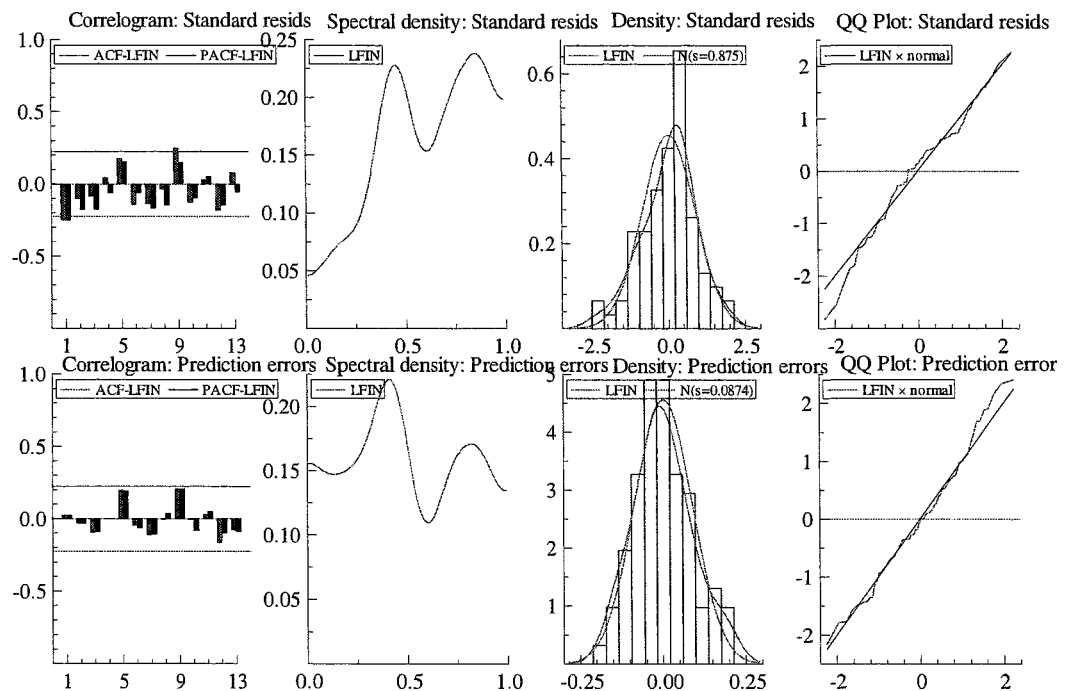
***Table 4.3.1.5: Regime Classification for Consumer Goods Industrial Sector***

Regime 1	Months Duration	Regime 2	Months Duration	Regime 3	Months Duration
1988:3 - 1994:1	84	1994:2 - 1999:4	69	1986:2 - 1988:2	27
2000:1 - 2005:4	60				

### 4.3.2 Mergers and Acquisitions Waves in Financial Companies Industrial Sector.

The model diagnostics are illustrated in Figure 4.3.2.1 and they suggest that the model is generally well-specified. There is a slight problem with serial correlation in the standardized residuals but this problem does not extend to the predictive errors, which all lie comfortably within the standard error bands. The density and QQ plots both suggest that the model is well-specified, as they are very close to normal distributions for both the standardized residuals and the predictive errors.

**Figure 4.3.2.1: Model Diagnostics for Financial Companies Industrial Sector**



The estimated coefficients for this model are given in Table 4.3.2.1.

**Table 4.3.2.1: Estimated Parameters from the Three Regimes for Financial Companies Industrial Sector**

<i>Regime Dependent Mean Values</i>	
$v_1$	-0.0185 (-2.5012) ***
$v_2$	-0.0122 (-1.6183) ***
$v_3$	0.0708 (7.2226) ***
<i>Autoregressive Coefficients <math>\theta_{im}</math></i>	
$\Delta y_{t-1}$	-1.1894 (-8.5580) ***
$\Delta y_{t-2}$	-1.2445 (-6.2416) ***
$\Delta y_{t-3}$	-0.7087 (-3.7196) ***
$\Delta y_{t-4}$	-0.3584 (-3.1415) *
***, **, * Denotes significance at 1%, 5% and 10% respectively	

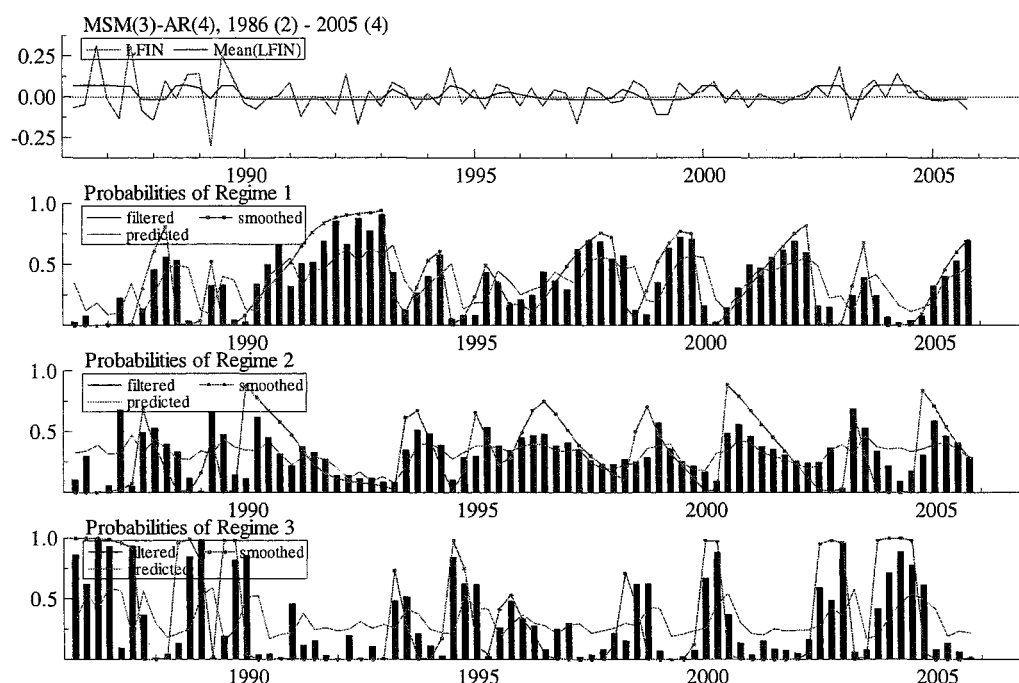
The mean values are clearly different, supporting the hypothesis that the series follows three distinct regimes over the sample period and the coefficients on the four lags are all statistically significant. The transition matrix for these regimes is given in table 4.3.2.2 and the regime probabilities are illustrated in 4.3.2.2.

**Table 4.3.2.2: Transition Probabilities for Financial Companies Industrial Sector**

	Regime 1	Regime 2	Regime 3
<b>Regime 1</b>	0.6992	0.0264	0.2745
<b>Regime 2</b>	0.2636	0.6442	0.0922
<b>Regime 3</b>	0.0861	0.3155	0.5984



**Figure 4.3.2.2: Regime Probabilities for Financial Companies Industrial Sector**



It is difficult to suggest that a dominant regime exist in the case of financial companies. When the series is in Regime 1 it is most likely to remain in that regime (69.92%), while the probability of the series flattening out and moving to Regime 2 is quite low (2.64%). Finally, it is considerably possible that the series will change directly from Regime 1 to Regime 3 (27.47%).

The probability that the series will remain in Regime 2, given that it is currently there, is quite high (64.42%). If the series deviates from Regime 2, it is more likely to move to Regime 1 (26.36%), than Regime 3. Finally, when the series is rising (Regime 3), it is more likely to remain in the same regime (59.84%). If the data

does not remain to Regime 3, it is most probable that it will move to Regime 2 (31.55%), than to Regime .1 (8.61%).

In addition to the transition probabilities, the expected duration for each of these regimes can also be calculated and appears in Table 4.3.2.3.

**Table 4.3.2.3: Durations of the Three Regimes for Financial Companies Industrial Sector**

	<i>Number of Observations</i>	<i>Ergodic Probability</i>	<i>Duration</i>
Regime 1	28.3	0.3659	3.32
Regime 2	24.9	0.3124	2.81
Regime 3	25.8	0.3218	2.49

The durations confirm the information supplied by the transition probabilities. The expected duration of Regime 1 is slightly longer than the durations of either of the other two regimes.

The results for the asymmetry tests reported in Table 4.3.2.4 and match our expectations. There is no evidence of differences in the sharpness or deepness of the periods in which the merger waves start and fall but there is evidence of significant differences in the steepness with which the waves begin and end. The null hypothesis of no difference in steepness is rejected at the 5% level, which supports the earlier supposition that merger waves begin more rapidly than they end.

**Table 4.3.2.4: Tests of Asymmetry for Financial Companies Industrial Sector**

<i>Test</i>	<i>Calculated Value</i>
<b>Sharpness Test</b>	0.1454
<b>Deepness Test</b>	1.1294
<b>Steepness Test</b>	0.2730

Finally, Table 4.3.2.5 presents the results for the regime classification process.

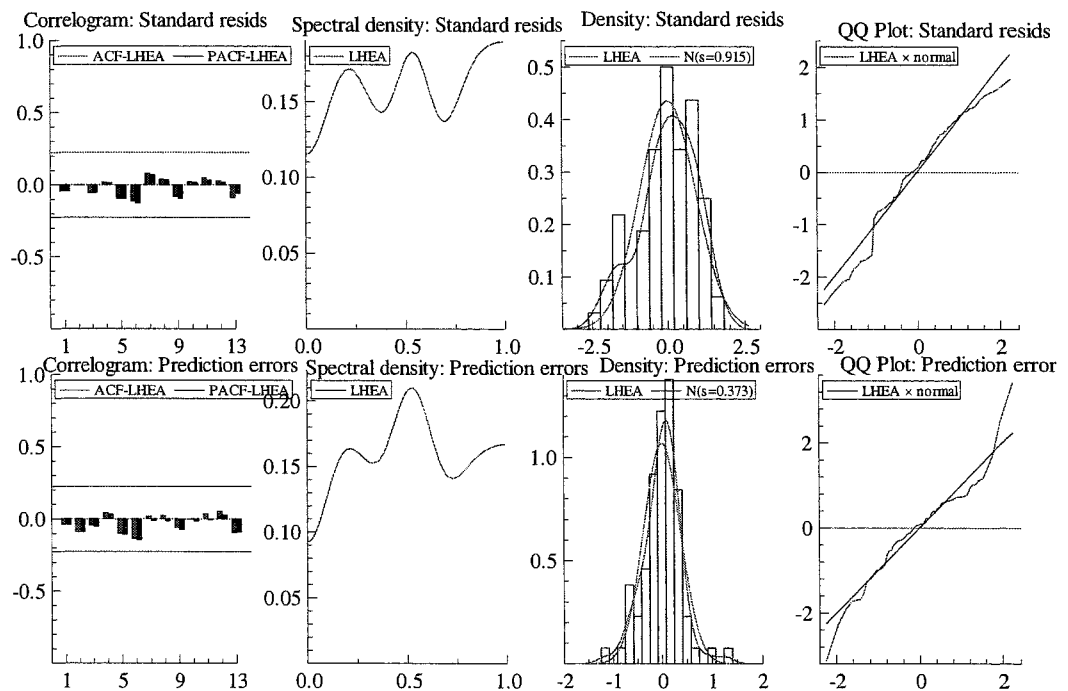
**Table 4.3.2.5: Regime Classification for Financial Companies Industrial Sector**

<b>Regime 1</b>	<b>Months Duration</b>	<b>Regime 2</b>	<b>Months Duration</b>	<b>Regime 3</b>	<b>Months Duration</b>
1988:1 - 1988:2	6	1987:4 - 1987:4	3	1986:2 - 1987:3	12
1989:2 - 1989:2	3	1990:1 - 1990:4	12	1988:3 - 1989:1	12
1991:1 - 1993:1	15	1993:3 - 1993:4	6	1989:3 - 1989:4	6
1994:1 - 1994:2	6	1995:1 - 1995:1	3	1993:2 - 1993:2	3
1995:2 - 1995:2	3	1996:1 - 1997:1	12	1994:3 - 1994:4	6
1997:2 - 1998:1	12	1998:3 - 1998:4	6	1995:3 - 1995:4	6
1999:1 - 1999:4	12	2000:3 - 2001:2	12	1998:2 - 1998:2	3
2001:3 - 2002:2	12	2003:2 - 2003:2	3	2000:1 - 2000:2	6
2003:3 - 2003:3	3	2004:4 - 2005:2	9	2002:3 - 2003:1	9
2005:3 - 2005:4	6			2003:4 - 2004:3	9

### 4.3.3 Mergers and Acquisitions Waves in Health Care Industrial Sector.

The model diagnostics are illustrated in Figure 4.3.3.1 and they suggest that the model is generally well-specified. The density and QQ plots both suggest that the model is well-specified, as they are very close to normal distributions for both the standardized residuals and the predictive errors.

**Figure 4.3.3.1: Model Diagnostics for Health Care Industrial Sector**



The estimated coefficients for this model are given in Table 4.3.3.1.

**Table 4.3.3.1: Estimated Parameters from the Three Regimes for Health Care Industrial Sector**

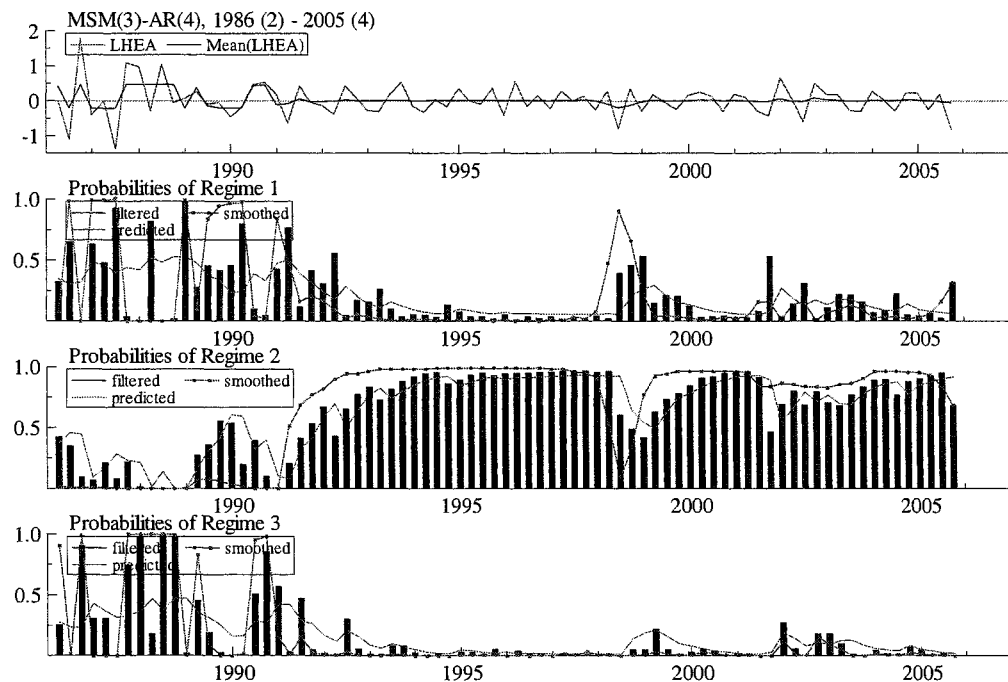
<i>Regime Dependent Mean Values</i>	
$v_1$	-0.2161 (-5.8835) ***
$v_2$	0.0156 (1.3454) ***
$v_3$	0.4665 (9.7008) ***
<i>Autoregressive Coefficients <math>\theta_{im}</math></i>	
$\Delta y_{t-1}$	-1.0534 (-10.7692) ***
$\Delta y_{t-2}$	-0.9424 (-8.8984) ***
$\Delta y_{t-3}$	-0.8129 (-7.6943) ***
$\Delta y_{t-4}$	-0.4197 (-4.8974) *
***, **, * Denotes significance at 1%, 5% and 10% respectively	

The mean values are clearly different, supporting the hypothesis that the series follows three distinct regimes over the sample period and the coefficients on the four lags are all statistically significant. The transition matrix for these regimes is given in table 4.3.3.2 and the regime probabilities are illustrated in Figure 4.3.3.2.

**Table 4.3.3.2: Transition Probabilities for Health Care Industrial Sector**

	Regime 1	Regime 2	Regime 3
Regime 1	0.4753	0.1684	0.3564
Regime 2	0.03944	0.9606	1.614e-009
Regime 3	0.5268	1.354e-005	0.4731

**Figure 4.3.3.2: Regime Probabilities for Health Care Industrial Sector**



It is clear that the dominant regime exist is Regime 2 (normal mergers and acquisitions activity). When the series is in Regime 1 it is more likely to remain in that regime (47.53%), while the probability of the series flattening out and moving to Regime 2 is significantly lower (16.84%). Finally, it is considerably possible that the series will change directly from Regime 1 to Regime 3 (35.64%).

The probability that the series will remain in Regime 2, given that it is currently there, is very high (96.06%). If the series deviates from Regime 2, it is most likely to move to Regime 1 (39.44%), than Regime 3. Finally, when the series is rising (Regime 3), it is more likely to move to Regime 1 (52.68%), while the probability of remaining in Regime 3, is 47.31%.

In addition to the transition probabilities, the expected duration for each of these regimes can also be calculated and appears in Table 4.3.3.3.

**Table 4.3.3.3: Durations of the Three Regimes for Health Care Industrial Sector**

	<i>Number of Observations</i>	<i>Ergodic Probability</i>	<i>Duration</i>
Regime 1	15.5	0.1682	1.91
Regime 2	52.6	0.7181	25.36
Regime 3	10.9	0.1138	1.90

The durations confirm the information supplied by the transition probabilities. The expected duration of Regime 2 is considerably longer than the durations of either of the other two regimes.

The results for the asymmetry tests reported in Table 4.3.3.4 and match our expectations. There is no evidence of differences in the sharpness or deepness of the periods in which the merger waves start and fall but there is evidence of significant differences in the steepness with which the waves begin and end. The null hypothesis of no difference in steepness is rejected at the 5% level, which supports the earlier supposition that merger waves begin more rapidly than they end.

**Table 4.3.3.4: Tests of Asymmetry for Health Care Industrial Sector**

<i>Test</i>	<i>Calculated Value</i>
Sharpness Test	0.0003
Deepness Test	8.8213
Steepness Test	7.8194

Finally, Table 4.3.3.5 presents the results for the regime classification process.

**Table 4.3.3.5: Regime Classification for Health Care Industrial Sector**

Regime 1	Months Duration	Regime 2	Months Duration	Regime 3	Months Duration
1986:3 - 1986:3	3	1991:2 - 1998:2	87	1986:2 - 1986:2	3
1987:1 - 1987:3	9	1999:1 - 2005:4	72	1986:4 - 1986:4	3
1989:1 - 1989:1	3			1987:4 - 1988:4	12
1989:3 - 1990:2	12			1989:2 - 1989:2	3
1991:1 - 1991:1	3			1990:3 - 1990:4	6
1998:3 - 1998:4	6				

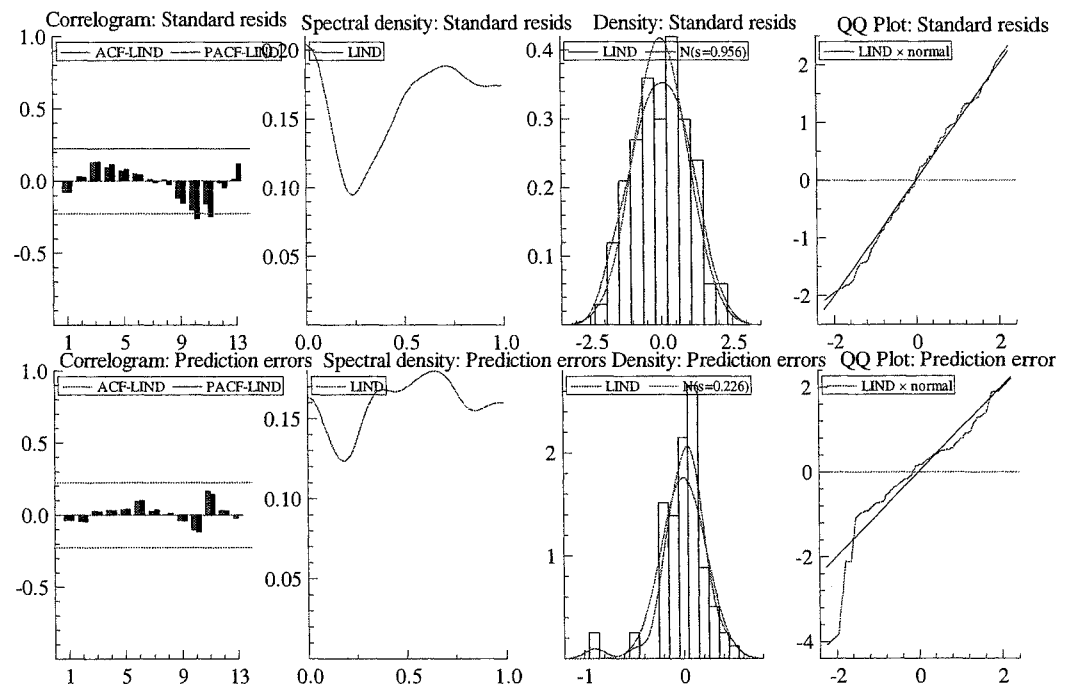
#### **4.3.4 Mergers and Acquisitions Waves in Industrial Companies Industrial Sector.**

The model diagnostics are illustrated in Figure 4.3.4.1 and they suggest that the model is generally well-specified. There is a slight problem with serial correlation in the standardized residuals but this problem does not extend to the predictive



errors, which all lie comfortably within the standard error bands. The density and QQ plots both suggest that the model is well-specified, as they are very close to normal distributions for both the standardized residuals and the predictive errors.

**Figure 4.3.4.1: Model Diagnostics for Industrial Companies Industrial Sector**



The estimated coefficients for this model are given in Table 4.3.4.1.

**Table 4.3.4.1: Estimated Parameters from the Three Regimes for Industrial Companies Industrial Sector**

Regime Dependent Mean Values	
$v_1$	-0.4827 (-8.9027) ***
$v_2$	-0.0116 (-1.7624) ***
$v_3$	0.3081 (10.8100) ***

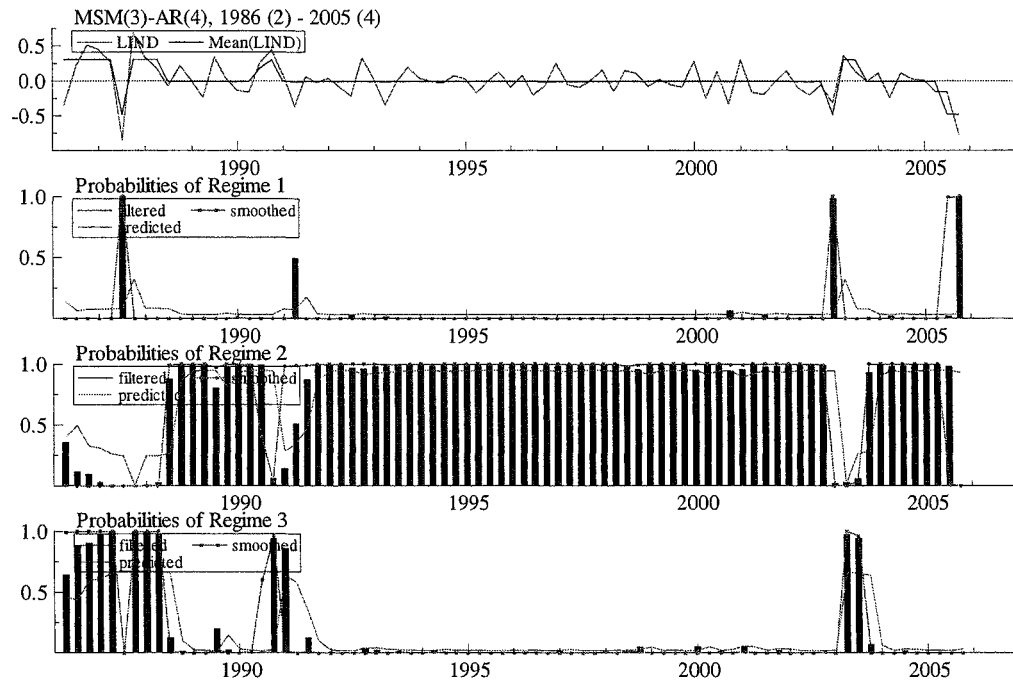
<i>Autoregressive Coefficients <math>\theta_{im}</math></i>	
$\Delta y_{t-1}$	-0.7033 (-8.9730)***
$\Delta y_{t-2}$	-0.6176 (-7.6888)***
$\Delta y_{t-3}$	-0.4009 (-5.2774)***
$\Delta y_{t-4}$	-0.0179 (-0.2721)*
***, **, * Denotes significance at 1%, 5% and 10% respectively	

The mean values are clearly different, supporting the hypothesis that the series follows three distinct regimes over the sample period and the coefficients on the four lags are all statistically significant. The transition matrix for these regimes is given in table 4.3.4.2 and the regime probabilities are illustrated in Figure 4.3.4.2.

**Table 4.3.4.2: Transition Probabilities for Industrial Companies Industrial Sector**

	<b>Regime 1</b>	<b>Regime 2</b>	<b>Regime 3</b>
<b>Regime 1</b>	0.3254	9.114e-006	0.6746
<b>Regime 2</b>	0.03184	0.9508	0.01735
<b>Regime 3</b>	0.08080	0.2446	0.6746

**Figure 4.3.4.2: Regime Probabilities for Industrial Companies Industrial Sector**



It is clear that the dominant regime exist is Regime 2 (normal mergers and acquisitions activity). When the series is in Regime 1 it is more likely to move to Regime 3 (67.46), than to remain in that regime (32.54%), while the probability of the series flattening out and moving to Regime 2 is almost non existent.

The probability that the series will remain in Regime 2, given that it is currently there, is very high (95.08%). If the series deviates from Regime 2, it is most likely to move to Regime 1 (3.184%), than Regime 3 (1.735%). Finally, when the series is rising (Regime 3), it is less likely to move to Regime 1 (8.08%), than Regime 2 (24.46%), while the probability of remaining in Regime 3, is 67.46%.

In addition to the transition probabilities, the expected duration for each of these regimes can also be calculated and appears in Table 4.3.4.3.

**Table 4.3.4.3: Durations of the Three Regimes for Industrial Companies  
Industrial Sector**

	<i>Number of Observations</i>	<i>Ergodic Probability</i>	<i>Duration</i>
Regime 1	4.0	0.0560	1.48
Regime 2	63.3	0.7859	20.33
Regime 3	11.6	0.1580	3.07

The durations confirm the information supplied by the transition probabilities. The expected duration of Regime 2 is considerably longer than the durations of either of the other two regimes.

The results for the asymmetry tests reported in Table 4.3.4.4 and match our expectations. There is no evidence of differences in the sharpness or deepness of the periods in which the merger waves start and fall but there is evidence of significant differences in the steepness with which the waves begin and end. The null hypothesis of no difference in steepness is rejected at the 5% level, which supports the earlier supposition that merger waves begin more rapidly than they end.

**Table 4.3.4.4: Tests of Asymmetry for Industrial Companies Industrial Sector**

<i>Test</i>	<i>Calculated Value</i>
<b>Sharpness Test</b>	0.1779
<b>Deepness Test</b>	9.7183
<b>Steepness Test</b>	14.0182

Finally, Table 4.3.4.5 presents the results for the regime classification process.

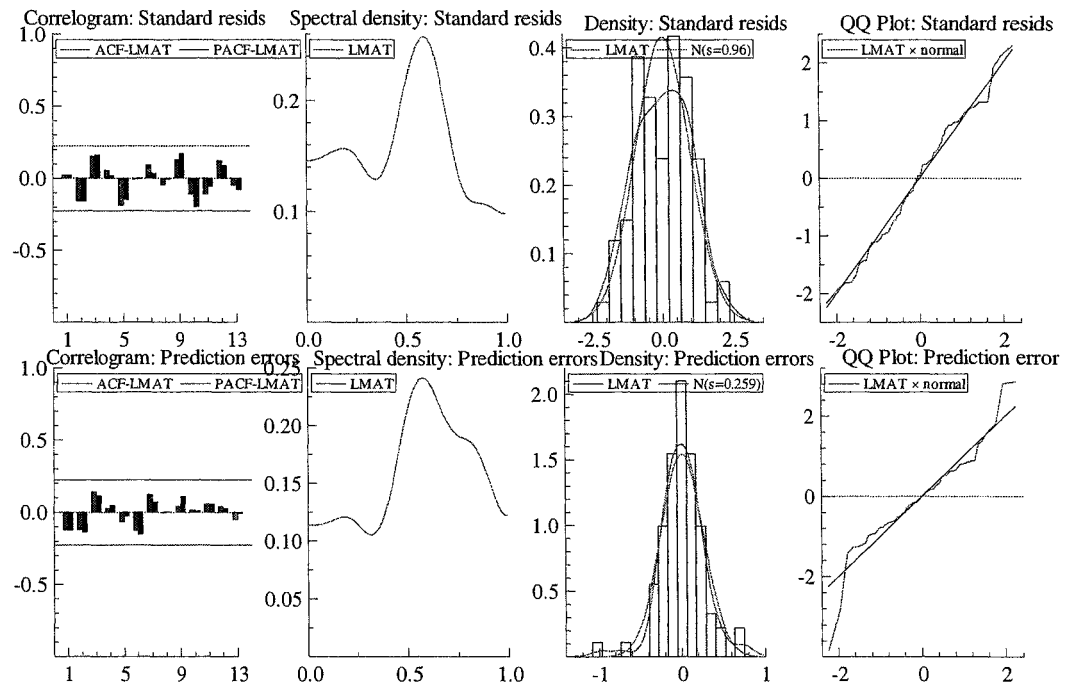
**Table 4.3.4.5: Regime Classification for Industrial Companies Industrial Sector**

<b>Regime 1</b>	<b>Months Duration</b>	<b>Regime 2</b>	<b>Months Duration</b>	<b>Regime 3</b>	<b>Months Duration</b>
1987:3 - 1987:3	3	1988:3 - 1990:2	24	1986:2 - 1987:2	12
2003:1 - 2003:1	3	1991:1 - 2002:4	132	1987:4 - 1988:2	9
2005:3 - 2005:4	6	2003:4 - 2005:2	21	1990:3 - 1990:4	6
				2003:2 - 2003:3	6

#### 4.3.5 Mergers and Acquisitions Waves in Basic Materials Industrial Sector.

The model diagnostics are illustrated in Figure 4.3.5.1 and they suggest that the model is generally well-specified. The density and QQ plots both suggest that the model is well-specified, as they are very close to normal distributions for both the standardized residuals and the predictive errors.

**Figure 4.3.5.1: Model Diagnostics for Basic Materials Industrial Sector**



The estimated coefficients for this model are given in Table 4.3.5.1.

**Table 4.3.5.1: Estimated Parameters from the Three Regimes for Basic Materials Industrial Sector**

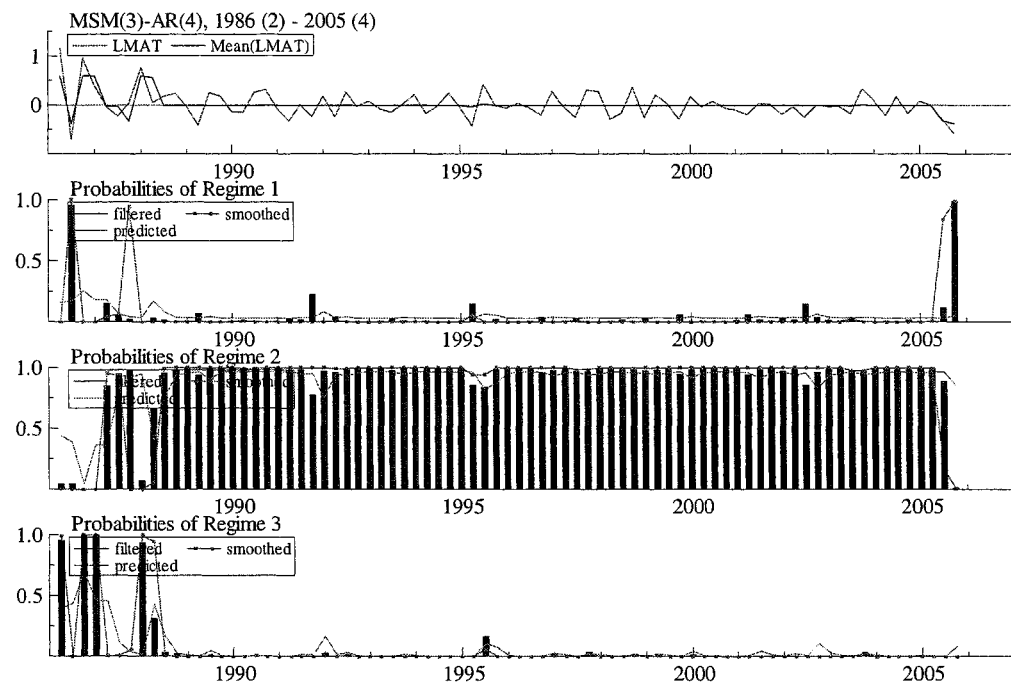
<i>Regime Dependent Mean Values</i>	
$v_1$	-0.3818 (-3.6387) ***
$v_2$	-0.0093 (-0.9005) ***
$v_3$	0.5958 (6.7204) ***
<i>Autoregressive Coefficients <math>\theta_{im}</math></i>	
$\Delta y_{t-1}$	-0.6044 (-3.7330) ***
$\Delta y_{t-2}$	-0.4061 (-2.1623) ***
$\Delta y_{t-3}$	-0.2160 (-2.1772) ***
$\Delta y_{t-4}$	0.0551 (0.5809) *
***, **, * Denotes significance at 1%, 5% and 10% respectively	

The mean values are clearly different, supporting the hypothesis that the series follows three distinct regimes over the sample period and the coefficients on the four lags are all statistically significant. The transition matrix for these regimes is given in table 4.3.5.2 and the regime probabilities are illustrated in Figure 4.3.5.2.

**Table 4.3.5.2: Transition Probabilities for Basic Materials Industrial Sector**

	<b>Regime 1</b>	<b>Regime 2</b>	<b>Regime 3</b>
<b>Regime 1</b>	0.2671	2.138e-012	0.7329
<b>Regime 2</b>	0.02972	0.9703	1.910e-005
<b>Regime 3</b>	0.1816	0.3594	0.4590

**Figure 4.3.5.2: Regime Probabilities for Basic Materials Industrial Sector**



It is clear that the dominant regime exist is Regime 2 (normal mergers and acquisitions activity). When the series is in Regime 1 it is more likely to move to Regime 3 (73.29), than to remain in that regime (26.71%), while the probability of the series flattening out and moving to Regime 2 is almost non existent.

The probability that the series will remain in Regime 2, given that it is currently there, is very high (97.03%). If the series deviates from Regime 2, it is most likely to move to Regime 1 (29.72%). Finally, when the series is rising (Regime 3), it is less likely to move to Regime 1 (18.16%), than Regime 2 (35.49%), while the most probable scenario is to remain in Regime 3 (45.90%).



In addition to the transition probabilities, the expected duration for each of these regimes can also be calculated and appears in Table 4.3.5.3.

**Table 4.3.5.3: Durations of the Three Regimes for Basic Materials Industrial Sector**

	<i>Number of Observations</i>	<i>Ergodic Probability</i>	<i>Duration</i>
Regime 1	4.0	0.0534	1.36
Regime 2	69.8	0.8743	33.62
Regime 3	5.1	0.0724	1.85

The durations confirm the information supplied by the transition probabilities. The expected duration of Regime 2 is considerably longer than the durations of either of the other two regimes.

The results for the asymmetry tests reported in Table 4.3.5.4 and match our expectations. There is no evidence of differences in the sharpness or deepness of the periods in which the merger waves start and fall but there is evidence of significant differences in the steepness with which the waves begin and end. The null hypothesis of no difference in steepness is rejected at the 5% level, which supports the earlier supposition that merger waves begin more rapidly than they end.

**Table 4.3.5.4: Tests of Asymmetry for Basic Materials Industrial Sector**

<i>Test</i>	<i>Calculated Value</i>
<b>Sharpness Test</b>	0.0488
<b>Deepness Test</b>	18.2762
<b>Steepness Test</b>	3.3049

Finally, Table 4.3.5.5 presents the results for the regime classification process.

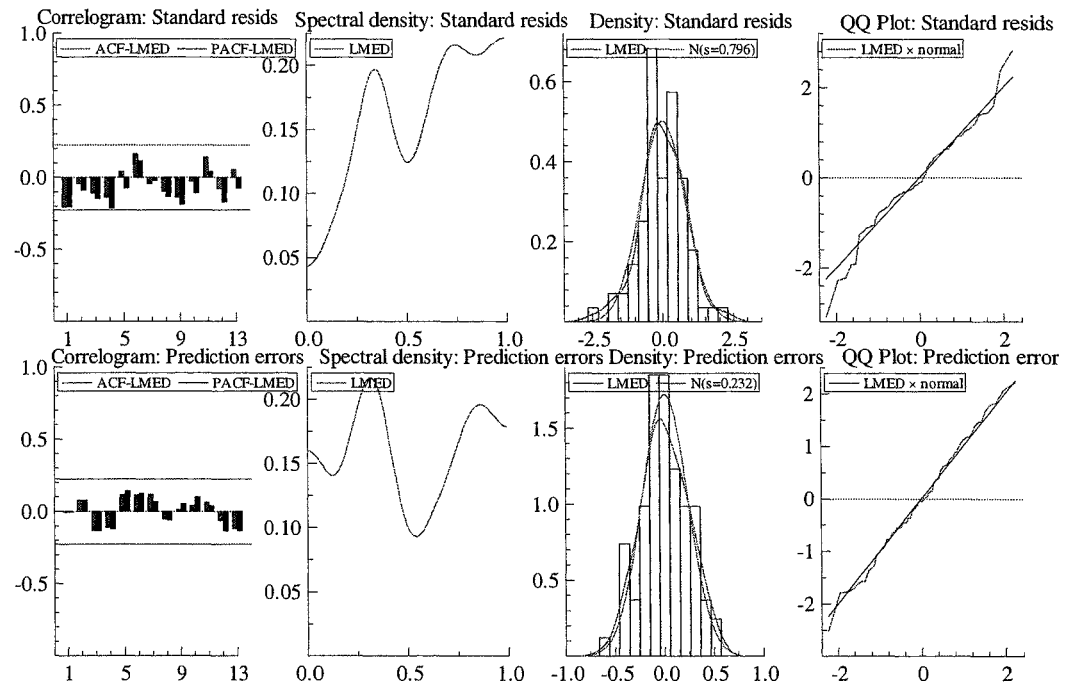
**Table 4.3.5.5: Regime Classification for Basic Materials Industrial Sector**

<b>Regime 1</b>	<b>Months Duration</b>	<b>Regime 2</b>	<b>Months Duration</b>	<b>Regime 3</b>	<b>Months Duration</b>
1986:3 - 1986:3	3	1987:2 - 1987:3	6	1986:2 - 1986:2	3
1987:4 - 1987:4	3	1988:3 - 2005:2	84	1986:4 - 1987:1	6
2005:3 - 2005:4	6			1988:1 - 1988:2	6

#### 4.3.6 Mergers and Acquisitions Waves in Media Companies Industrial Sector.

The model diagnostics are illustrated in Figure 4.3.6.1 and they suggest that the model is generally well-specified. The density and QQ plots both suggest that the model is well-specified, as they are very close to normal distributions for both the standardized residuals and the predictive errors.

**Figure 4.3.6.1: Model Diagnostics for Media Companies Industrial Sector**



The estimated coefficients for this model are given in Table 4.3.6.1.

**Table 4.3.6.1: Estimated Parameters from the Three Regimes for Media Companies Industrial Sector**

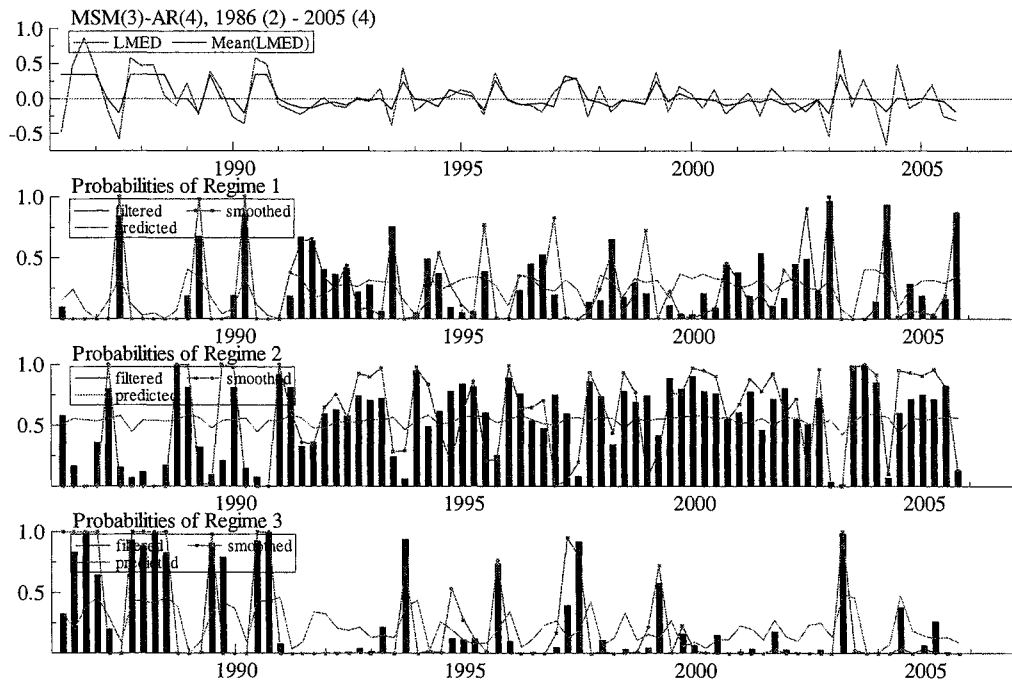
<i>Regime Dependent Mean Values</i>	
$v_1$	-0.2067 (-4.3539) ***
$v_2$	-0.0012 (-0.0514) ***
$v_3$	0.3482 (9.6958) ***
<i>Autoregressive Coefficients <math>\theta_{im}</math></i>	
$\Delta y_{t-1}$	-0.8703 (-8.7848) ***
$\Delta y_{t-2}$	--0.8967 (-9.5033) ***
$\Delta y_{t-3}$	-0.5985 (-7.4939) ***
$\Delta y_{t-4}$	-0.4155 (-5.6813) *
***, **, * Denotes significance at 1%, 5% and 10% respectively	

The mean values are clearly different, supporting the hypothesis that the series follows three distinct regimes over the sample period and the coefficients on the four lags are all statistically significant. The transition matrix for these regimes is given in table 4.3.6.2 and the regime probabilities are illustrated in Figure 4.3.6.2.

**Table 4.3.6.2: Transition Probabilities for Media Companies Industrial Sector**

	<b>Regime 1</b>	<b>Regime 2</b>	<b>Regime 3</b>
<b>Regime 1</b>	0.06919	0.4220	0.5088
<b>Regime 2</b>	0.4079	0.5921	1.330e-011
<b>Regime 3</b>	5.661e-006	0.5360	0.4640

**Figure 4.3.6.2: Regime Probabilities for Media Companies Industrial Sector**



It is clear that the dominant regime exist is Regime 2 (normal mergers and acquisitions activity). When the series is in Regime 1 it is more likely to move to Regime 3 (50.88), than to remain in that regime (6.919%), while the probability of the series flattening out and moving to Regime 2 is 42.20%.

The probability that the series will remain in Regime 2, given that it is currently there, is quite high (59.21%). If the series deviates from Regime 2, it is most likely to move to Regime 1 (40.79%). Finally, when the series is rising (Regime 3), it is less likely to remain in Regime 3 (46.40%), than moving to Regime 2 (53.60%), while the probability of moving to Regime 1 is extremely low.

In addition to the transition probabilities, the expected duration for each of these regimes can also be calculated and appears in Table 4.3.6.3.

**Table 4.3.6.3: Durations of the Three Regimes for Media Companies Industrial Sector**

	<i>Number of Observations</i>	<i>Ergodic Probability</i>	<i>Duration</i>
Regime 1	18.6	0.2364	1.07
Regime 2	42.7	0.5393	2.45
Regime 3	17.7	0.2244	1.87

The durations confirm the information supplied by the transition probabilities. The expected duration of Regime 2 is longer than the durations of either of the other two regimes.

The results for the asymmetry tests reported in Table 4.3.6.4 and match our expectations. There is no evidence of differences in the sharpness or deepness of the periods in which the merger waves start and fall but there is evidence of significant differences in the steepness with which the waves begin and end. The null hypothesis of no difference in steepness is rejected at the 5% level, which supports the earlier supposition that merger waves begin more rapidly than they end.

**Table 4.3.6.4: Tests of Asymmetry for Media Companies Industrial Sector**

<i>Test</i>	<i>Calculated Value</i>
<b>Sharpness Test</b>	0.0000
<b>Deepness Test</b>	8.6292
<b>Steepness Test</b>	4.8163

Finally, Table 4.3.6.5 presents the results for the regime classification process.

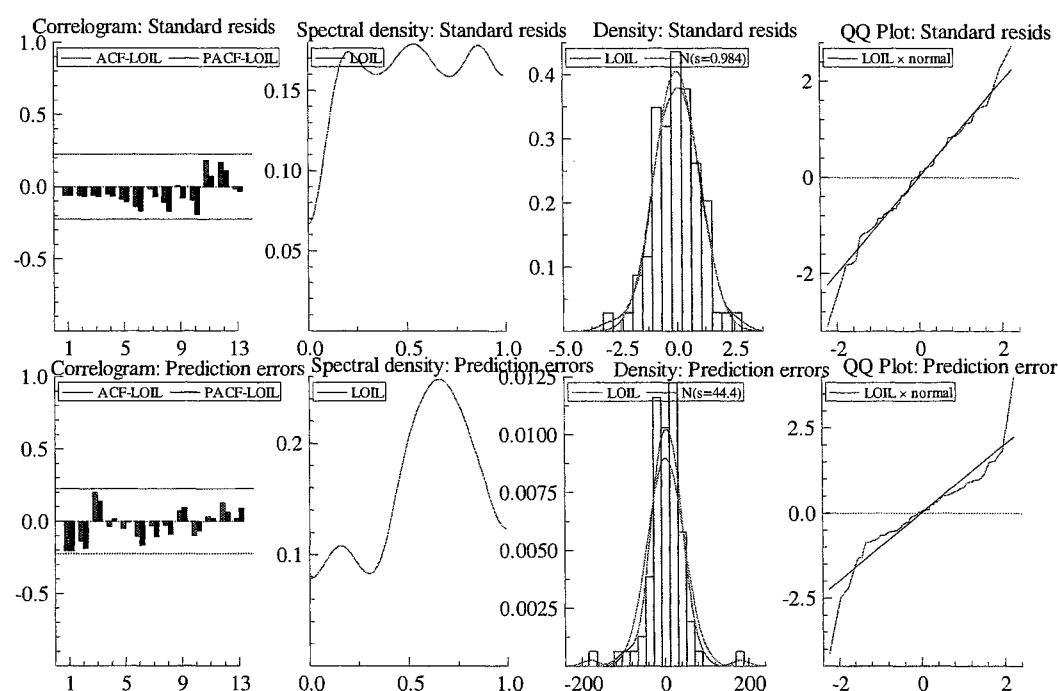
**Table 4.3.6.5: Regime Classification for Media Companies Industrial Sector**

Regime 1	Months Duration	Regime 2	Months Duration	Regime 3	Months Duration
1987:3 - 1987:3	3	1987:2 - 1987:2	3	1986:2 - 1987:1	12
1989:2 - 1989:2	3	1988:4 - 1989:1	6	1987:4 - 1988:3	12
1990:2 - 1990:2	3	1989:4 - 1990:1	6	1989:3 - 1989:3	3
1991:3 - 1991:4	6	1991:1 - 1991:2	6	1990:3 - 1990:4	6
1993:3 - 1993:3	3	1992:1 - 1993:2	15	1993:4 - 1993:4	3
1994:3 - 1994:3	3	1994:1 - 1994:2	6	1994:4 - 1994:4	3
1995:3 - 1995:3	3	1995:1 - 1995:2	6	1995:4 - 1995:4	3
1997:1 - 1997:1	3	1996:1 - 1996:4	12	1997:2 - 1997:3	6
1998:2 - 1998:2	3	1997:4 - 1998:1	6	1999:2 - 1999:2	3
1999:1 - 1999:1	3	1998:3 - 1998:4	6		
2002:3 - 2002:3	3	1999:3 - 2002:2	21		
2003:1 - 2003:1	3	2002:4 - 2002:4	3		
2004:2 - 2004:2	3	2003:3 - 2004:1	9		
2005:4 - 2005:4	3	2004:3 - 2005:3	12		

### 4.3.7 Mergers and Acquisitions Waves in Oil and Gas Companies Industrial Sector.

The model diagnostics are illustrated in Figure 4.3.7.1 and they suggest that the model is generally well-specified. The density and QQ plots both suggest that the model is well-specified, as they are very close to normal distributions for both the standardized residuals and the predictive errors.

**Figure 4.3.7.1: Model Diagnostics for Oil and Gas Companies Industrial Sector**



The estimated coefficients for this model are given in Table 4.3.7.1.



**Table 4.3.7.1: Estimated Parameters from the Three Regimes for Oil and Gas Companies Industrial Sector**

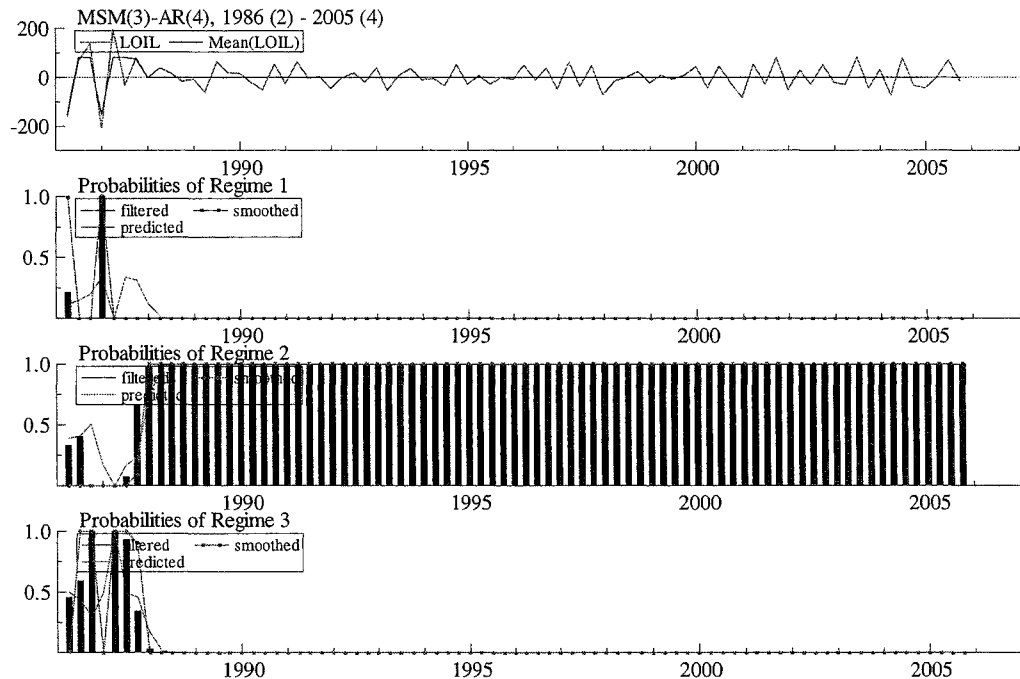
<i>Regime Dependent Mean Values</i>	
$v_1$	-152.9253 (-5.6312) ***
$v_2$	0.2794 (0.2227) ***
$v_3$	81.9057 (7.0453) ***
<i>Autoregressive Coefficients <math>\theta_{im}</math></i>	
$\Delta y_{t-1}$	-0.7715 (-8.0763) ***
$\Delta y_{t-2}$	-0.4022 (-3.0641) ***
$\Delta y_{t-3}$	-0.5550 (-4.7187) ***
$\Delta y_{t-4}$	-0.2880 (-3.2443) *
***, **, * Denotes significance at 1%, 5% and 10% respectively	

The mean values are clearly different, supporting the hypothesis that the series follows three distinct regimes over the sample period and the coefficients on the four lags are all statistically significant. The transition matrix for these regimes is given in table 4.3.7.2 and the regime probabilities are illustrated in Figure 4.3.7.2.

**Table 4.3.7.2: Transition Probabilities for Oil and Gas Companies Industrial Sector**

	<b>Regime 1</b>	<b>Regime 2</b>	<b>Regime 3</b>
<b>Regime 1</b>	1.419e-009	6.351e-014	1.000
<b>Regime 2</b>	5.521e-006	1.000	2.077e-009
<b>Regime 3</b>	0.3384	0.1695	0.4921

**Figure 4.3.7.2: Regime probabilities for Oil and Gas Companies Industrial Sector**



It is clear that a dominant regime exists and this is Regime 2 (normal mergers and acquisitions activity). When the series is in Regime 1 it is expected to move to Regime 3. Moreover it is expected to remain in Regime 2, given that it is currently there. Finally, when the series is rising (Regime 3), it is more likely to remain in Regime 3 (49.21%), than moving to Regime 1 (33.84%), or moving to Regime 2 (16.95%).

In addition to the transition probabilities, the expected duration for each of these regimes can also be calculated and appears in Table 4.3.7.3.

**Table 4.3.7.3: Durations of the Three Regimes for Oil and Gas Companies Industrial Sector**

	<i>Number of Observations</i>	<i>Ergodic Probability</i>	<i>Duration</i>
Regime 1	2.0	0.0000	1.00
Regime 2	72.1	1.0000	181046.18
Regime 3	4.9	0.0000	1.97

The durations confirm the information supplied by the transition probabilities. The expected duration of Regime 2 is longer than the durations of either of the other two regimes.

The results for the asymmetry tests reported in Table 4.4.7.4 and match our expectations. There is no evidence of differences in the sharpness or deepness of the periods in which the merger waves start and fall but there is evidence of significant differences in the steepness with which the waves begin and end. The null hypothesis of no difference in steepness is rejected at the 5% level, which supports the earlier supposition that merger waves begin more rapidly than they end.

**Table 4.3.7.4: Tests of Asymmetry for Oil and Gas Companies Industrial Sector**

<i>Test</i>	<i>Calculated Value</i>
<b>Sharpness Test</b>	0.0179
<b>Deepness Test</b>	0.8824

**Steepness Test**

4.6698

Finally, Table 4.3.7.5 presents the results for the regime classification process.

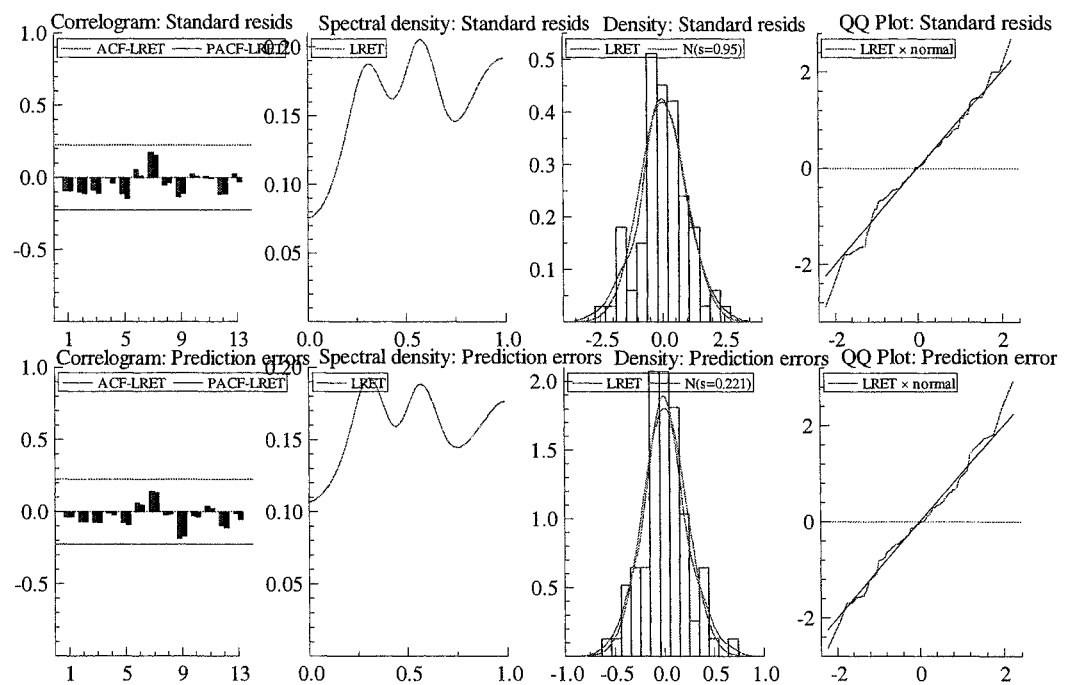
***Table 4.3.7.5: Regime Classification for Oil and Gas Companies Industrial Sector***

Regime 1	Months Duration	Regime 2	Months Duration	Regime 3	Months Duration
1986:2 - 1986:2	3	1988:1 - 2005:4	216	1986:3 - 1986:4	6
1987:1 - 1987:1	3			1987:2 - 1987:4	9

#### 4.3.8 Mergers and Acquisitions Waves in Retail Companies Industrial Sector.

The model diagnostics are illustrated in Figure 4.3.8.1 and they suggest that the model is generally well-specified. The density and QQ plots both suggest that the model is well-specified, as they are very close to normal distributions for both the standardized residuals and the predictive errors.

**Figure 4.3.8.1: Model Diagnostics for Retail Companies Industrial Sector**



The estimated coefficients for this model are given in Table 4.3.8.1.

**Table 4.3.8.1: Estimated Parameters from the Three Regimes for Retail Companies Industrial Sector**

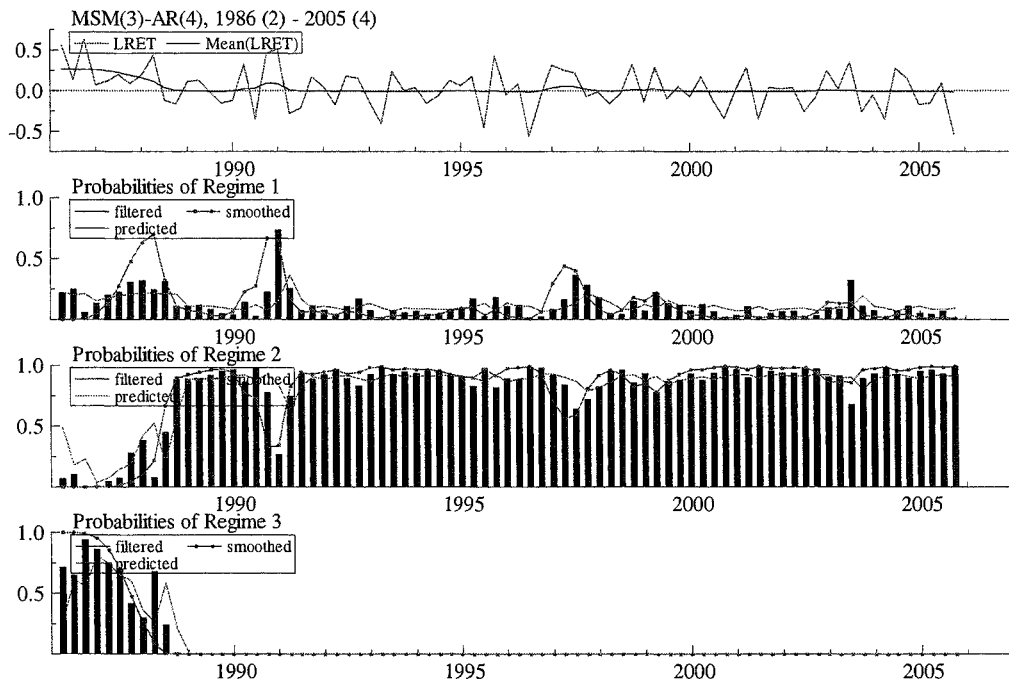
<i>Regime Dependent Mean Values</i>	
$v_1$	0.1410 (0.9999) ***
$v_2$	-0.0155 (-0.4626) ***
$v_3$	0.2622 (0.0363) ***
<i>Autoregressive Coefficients <math>\theta_{im}</math></i>	
$\Delta y_{t-1}$	-0.4278 (-2.0734) ***
$\Delta y_{t-2}$	-0.3642 (-1.8173) ***
$\Delta y_{t-3}$	-0.2883 (-1.5963) ***
$\Delta y_{t-4}$	-0.0825 (-0.5491) *
***, **, * Denotes significance at 1%, 5% and 10% respectively	

The mean values are clearly different, supporting the hypothesis that the series follows three distinct regimes over the sample period and the coefficients on the four lags are all statistically significant. The transition matrix for these regimes is given in table 4.3.8.2 and the regime probabilities are illustrated in Figure 4.3.8.2.

**Table 4.3.8.2: Transition Probabilities for Retail Companies Industrial Sector**

	<b>Regime 1</b>	<b>Regime 2</b>	<b>Regime 3</b>
<b>Regime 1</b>	0.4749	0.5251	5.955e-010
<b>Regime 2</b>	0.06380	0.9362	3.513e-012
<b>Regime 3</b>	0.1340	1.755e-005	0.8660

**Figure 4.3.8.2: Regime Probabilities for Retail Companies Industrial Sector**



It is clear that the dominant regime existing is Regime 2 (normal mergers and acquisitions activity). When the series is in Regime 1 it is more likely to move to Regime 2 (52.51%), than remaining in Regime 1 (47.49%), while there is almost no probability to move to Regime 3. Moreover it is expected to remain in Regime 2, given that it is currently there. Finally, when the series is rising (Regime 3), it is more likely to remain in Regime 3 (86.60%), than moving to Regime 1 (13.40%), or moving to Regime 2.

In addition to the transition probabilities, the expected duration for each of these regimes can also be calculated and appears in Table 4.3.8.3.

**Table 4.3.8.3: Durations of the Three Regimes for Retail Companies Industrial Sector**

	<i>Number of Observations</i>	<i>Ergodic Probability</i>	<i>Duration</i>
Regime 1	9.2	0.1083	1.90
Regime 2	63.4	0.8917	15.67
Regime 3	6.3	0.0000	7.46

The durations confirm the information supplied by the transition probabilities. The expected duration of Regime 2 is longer than the durations of either of the other two regimes.

The results for the asymmetry tests reported in Table 4.3.8.4 and match our expectations. There is no evidence of differences in the sharpness or deepness of the periods in which the merger waves start and fall but there is evidence of significant differences in the steepness with which the waves begin and end. The null hypothesis of no difference in steepness is rejected at the 5% level, which supports the earlier supposition that merger waves begin more rapidly than they end.

**Table 4.3.8.4: Tests of Asymmetry for Retail Companies Industrial Sector**

<i>Test</i>	<i>Calculated Value</i>
<b>Sharpness Test</b>	0.0067
<b>Deepness Test</b>	0.0021



**Steepness Test**

0.0001

Finally, Table 4.3.8.5 presents the results for the regime classification process.

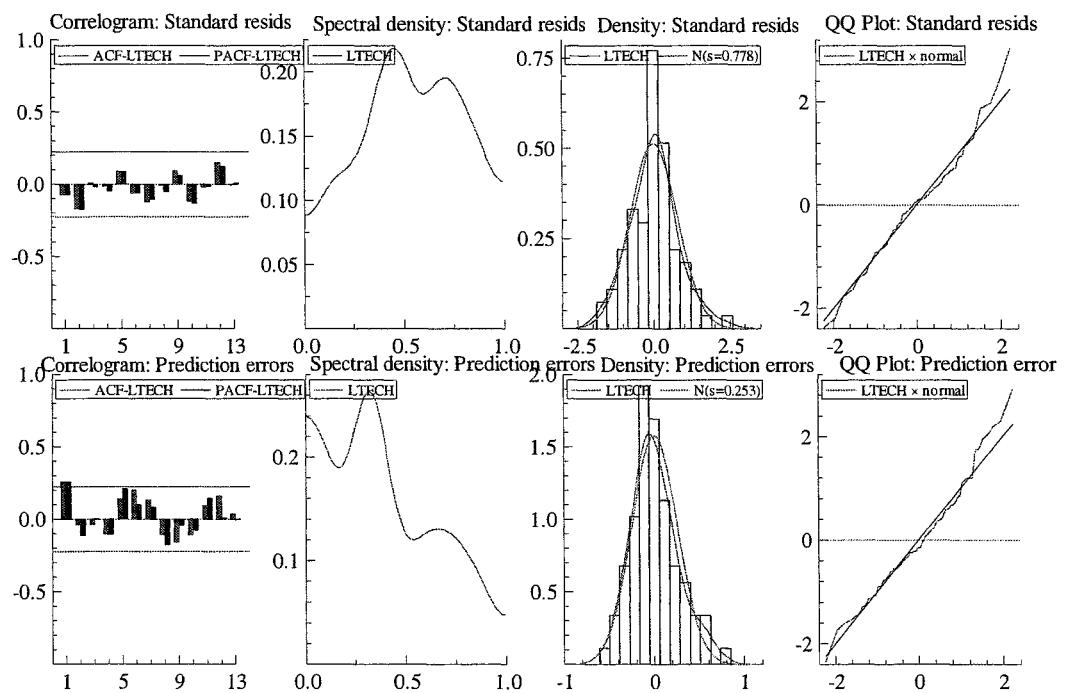
***Table 4.3.8.5: Regime Classification for Retail Companies Industrial Sector***

Regime 1	Months Duration	Regime 2	Months Duration	Regime 3	Months Duration
1987:4 - 1988:2	6	1988:3 - 1990:3	27	1986:2 - 1987:3	12
1990:4 - 1991:1	6	1991:2 - 2005:4	161		

### 4.3.9 Mergers and Acquisitions Waves in High Technology Companies Industrial Sector.

The model diagnostics are illustrated in Figure 4.3.9.1 and they suggest that the model is generally well-specified, although there is a slight problem with serial correlation in the predictive errors. The density and QQ plots both suggest that the model is well-specified, as they are very close to normal distributions for both the standardized residuals and the predictive errors.

**Figure 4.3.9.1: Model Diagnostics for High Technology Companies Industrial Sector**



The estimated coefficients for this model are given in Table 4.3.9.1.

**Table 4.3.9.1: Estimated Parameters from the Three Regimes Diagnostics for High Technology Companies Industrial Sector**

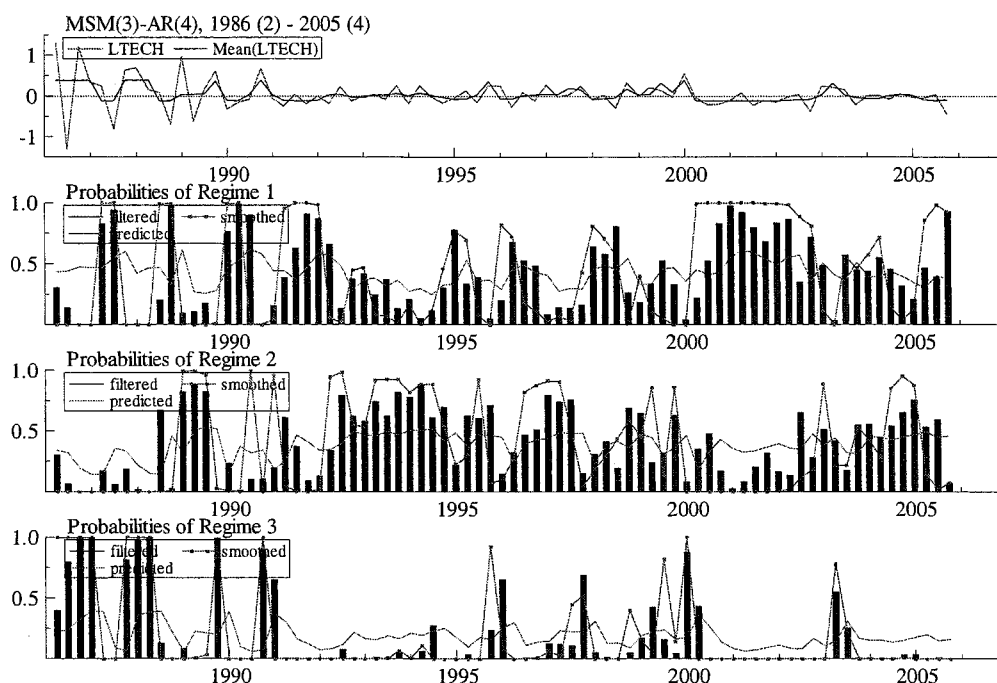
<i>Regime Dependent Mean Values</i>	
$v_1$	-0.1105 (-13.9966) ***
$v_2$	0.0388 (5.6201) ***
$v_3$	0.3858 (22.8569) ***
<i>Autoregressive Coefficients <math>\theta_{im}</math></i>	
$\Delta y_{t-1}$	-1.6596 (-27.4706) ***
$\Delta y_{t-2}$	-1.6540 (-22.0560) ***
$\Delta y_{t-3}$	-1.2287 (-17.6540) ***
$\Delta y_{t-4}$	-0.5313 (-11.0181) *
***, **, * Denotes significance at 1%, 5% and 10% respectively	

The mean values are clearly different, supporting the hypothesis that the series follows three distinct regimes over the sample period and the coefficients on the four lags are all statistically significant. The transition matrix for these regimes is given in table 4.3.9.2 and the regime probabilities are illustrated in Figure 4.3.9.2.

**Table 4.3.9.2: Transition Probabilities Diagnostics for High Technology Companies Industrial Sector**

	<b>Regime 1</b>	<b>Regime 2</b>	<b>Regime 3</b>
<b>Regime 1</b>	0.6247	0.3176	0.0577
<b>Regime 2</b>	0.2096	0.5622	0.2281
<b>Regime 3</b>	0.4694	0.1420	0.3885

**Figure 4.3.9.2: Regime Probabilities for High Technology Companies Industrial Sector**



In this case Regime 1 seems to be the dominant one. When the series is in Regime 1 it is less likely to move to Regime 2 (31.76%), than remaining in Regime 1 (62.47%), while there is a probability to move to Regime 3 (5.77%). Moreover it is expected to remain in Regime 2, given that it is currently there (56.22%), however in case it moves it is a bit more likely to move to Regime 3 (22.81%), than to Regime 1 (20.96%). Finally, when the series is rising (Regime 3), it is less likely to remain in Regime 3 (38.85%), than moving to Regime 1 (46.94%). The probability of moving to Regime 2 is 14.20%.

In addition to the transition probabilities, the expected duration for each of these regimes can also be calculated and appears in Table 4.3.9.3.

**Table 4.3.9.3: Durations of the Three Regimes Diagnostics for High Technology Companies Industrial Sector**

	<i>Number of Observations</i>	<i>Ergodic Probability</i>	<i>Duration</i>
Regime 1	34.7	0.4394	2.66
Regime 2	29.5	0.3780	2.28
Regime 3	14.8	0.1825	1.64

The durations confirm the information supplied by the transition probabilities. The expected duration of Regime 2 is longer than the durations of either of the other two regimes.

The results for the asymmetry tests reported in Table 4.3.9.4 and match our expectations. There is no evidence of differences in the sharpness or deepness of the periods in which the merger waves start and fall but there is evidence of significant differences in the steepness with which the waves begin and end. The null hypothesis of no difference in steepness is rejected at the 5% level, which supports the earlier supposition that merger waves begin more rapidly than they end.

**Table 4.3.9.4: Tests of Asymmetry Diagnostics for High Technology Companies Industrial Sector**

<i>Test</i>	<i>Calculated Value</i>
Sharpness Test	0.0168
Deepness Test	18.4181

Finally, Table 4.3.9.5 presents the results for the regime classification process.

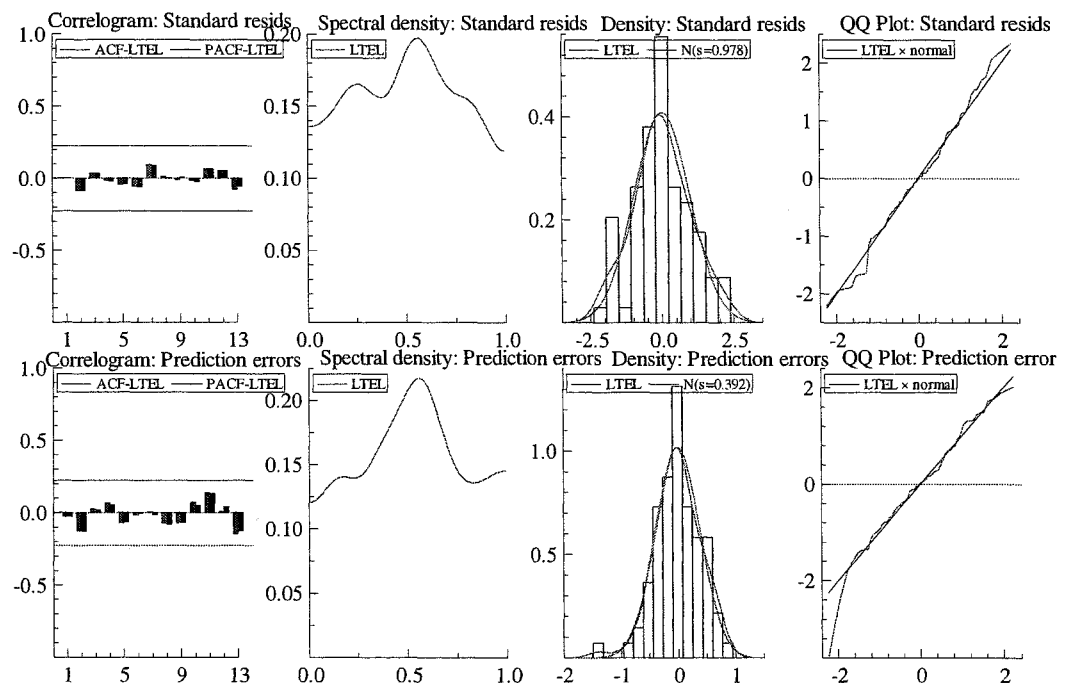
**Table 4.3.9.5: Regime Classification Diagnostics for High Technology Companies Industrial Sector**

Regime 1	Months Duration	Regime 2	Months Duration	Regime 3	Months Duration
1987:2 - 1987:3	6	1989:1 - 1989:3	9	1986:2 - 1987:1	12
1988:3 - 1988:4	6	1990:3 - 1990:3	3	1987:4 - 1988:2	15
1990:1 - 1990:2	6	1991:1 - 1991:1	3	1989:4 - 1989:4	3
1991:2 - 1992:1	12	1992:2 - 1994:4	12	1990:4 - 1990:4	3
1995:1 - 1995:2	6	1995:3 - 1995:3	3	1995:4 - 1995:4	3
1996:1 - 1996:2	6	1996:3 - 1997:3	12	1997:4 - 1997:4	3
1998:1 - 1998:3	9	1998:4 - 1999:2	9	1999:3 - 1999:3	3
2000:2 - 2002:4	9	1999:4 - 1999:4	3	2000:1 - 2000:1	3
2003:3 - 2003:3	3	2003:1 - 2003:1	3	2003:2 - 2003:2	3
2004:1 - 2004:2	6	2003:4 - 2003:4	3		
2005:2 - 2005:4	9	2004:3 - 2005:1	12		

#### 4.3.10 Mergers and Acquisitions Waves in Telecommunication Companies Industrial Sector.

The model diagnostics are illustrated in Figure 4.3.10.1 and they suggest that the model is generally well-specified, although there is a slight problem with serial correlation in the predictive errors. The density and QQ plots both suggest that the model is well-specified, as they are very close to normal distributions for both the standardized residuals and the predictive errors.

**Figure 4.3.10.1: Model Diagnostics for Telecommunication Companies Industrial Sector**



The estimated coefficients for this model are given in Table 4.3.10.1.

**Table 4.3.10.1: Estimated Parameters from the Three Regimes for Telecommunication Companies Industrial Sector**

<b>Regime Dependent Mean Values</b>	
$v_1$	-0.7964 (-3.6696) ***
$v_2$	0.0068 (0.3923) ***
$v_3$	0.3947 4.0794) ***
<b>Autoregressive Coefficients <math>\theta_{im}</math></b>	
$\Delta y_{t-1}$	-0.8902 (-7.6792) ***
$\Delta y_{t-2}$	-0.5024 (-3.5096) ***
$\Delta y_{t-3}$	-0.3058 (-2.1393) ***
$\Delta y_{t-4}$	-0.2069 (-1.9017) *
***, **, * Denotes significance at 1%, 5% and 10% respectively	

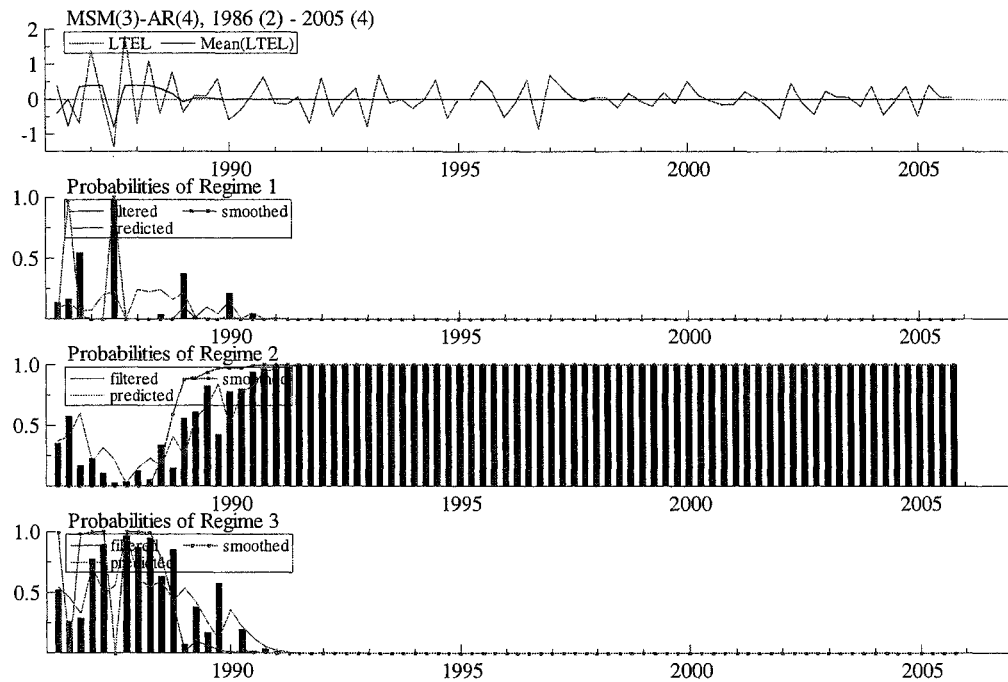
The mean values are clearly different, supporting the hypothesis that the series follows three distinct regimes over the sample period and the coefficients on the four lags are all statistically significant. The transition matrix for these regimes is given in table 4.3.10.2 and the regime probabilities are illustrated in Figure 4.3.10.2.

**Table 4.3.10.2: Transition Probabilities for Telecommunication Companies Industrial Sector**

	<b>Regime 1</b>	<b>Regime 2</b>	<b>Regime 3</b>
<b>Regime 1</b>	1.059e-010	1.205e-012	1.000
<b>Regime 2</b>	2.603e-009	1.000	2.944e-007
<b>Regime 3</b>	0.2544	0.1184	0.6272



**Figure 4.3.10.2: Regime Probabilities for Telecommunication Companies Industrial Sector**



In this case there exists practically one regime, Regime 2 (normal merger activity). When the series is in Regime 1 it is expected to move to Regime 3, while when it is in Regime 2 it is expected to remain in Regime 2. Finally, when the series is rising (Regime 3), it is more likely to remain in Regime 3 (62.72%), than moving to Regime 1 (25.44%). The probability of moving to Regime 2 is 11.84%.

In addition to the transition probabilities, the expected duration for each of these regimes can also be calculated and appears in Table 4.3.10.3.

**Table 4.3.10.3: Durations of the Three Regimes for Telecommunication Companies Industrial Sector**

	<i>Number of</i>	<i>Ergodic</i>	
	<i>Observations</i>	<i>Probability</i>	<i>Duration</i>
Regime 1	2.1	0.0000	1.00
Regime 2	68.4	1.0000	3366660.30
Regime 3	8.4	0.0000	2.68

The durations confirm the information supplied by the transition probabilities. The expected duration of Regime 2 is longer than the durations of either of the other two regimes.

The results for the asymmetry tests reported in Table 4.3.10.4 and match our expectations. There is no evidence of differences in the sharpness or deepness of the periods in which the merger waves start and fall but there is evidence of significant differences in the steepness with which the waves begin and end. The null hypothesis of no difference in steepness is rejected at the 5% level, which supports the earlier supposition that merger waves begin more rapidly than they end.

**Table 4.3.10.4: Tests of Asymmetry for Telecommunication Companies Industrial Sector**

<i>Test</i>	<i>Calculated Value</i>
Sharpness Test	0.2193

**Deepness Test** 2.8690

**Steepness Test** 1.8406

Finally, Table 4.3.10.5 presents the results for the regime classification process.

**Table 4.3.10.5: Regime Classification for Telecommunication Companies Industrial Sector**

Regime 1	Months Duration	Regime 2	Months Duration	Regime 3	Months Duration
1986:3 - 1986:3	3	1988:4 - 2005:4	227	1986:2 - 1986:2	3
1987:3 - 1987:3	3			1986:4 - 1987:2	12
				1987:4 - 1988:3	12

#### ***4.4 Relationship between Mergers and Acquisitions activity, the Stock Market and the Business Cycle***

The last part of this chapter attempts to identify a positive significant relationship between the mergers and acquisitions activity, the stock market and the business cycle. In order to do so a switching regression model, in which the mergers activity is assumed to switch between three regimes, is employed. The three regimes follow the classification identified in the previous section and characterised by periods of “falling”, “normal” and “rising” mergers activity respectively. The model takes the following form:

$$y_t = a_0 + a_1D_1 + a_3D_3 + \gamma_1D_1x_t + \gamma_3D_3x_t + \beta_0x_t + \delta_0\psi_t + \kappa_1D_1\psi_t + \kappa_3D_3\psi_t + u_t \quad (4.1)$$

Where,

$x_t$  is the relevant FTSE-ALL SHARES industrial stock market index(Consumer Products and Services, Financial companies, Healthcare, Industrials, Materials, Media and Entertainment, Retail, High Technology, Telecommunications and Oil and Gas )<sup>8</sup>;

$\psi_t$  is the UK Business Cycle Coincident Index<sup>9</sup>;

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<sup>8</sup> Downloaded from Datastream

<sup>9</sup> The UK Business Cycle Coincident Index has obtained from the Business Cycle Research Institute and used in this chapter with their permission

$D_1$ ,  $D_3$  are dummy variables.  $D_1$  is equal to one in regime one (i.e. in decreasing mergers activity periods at the end of a merger wave) and equal to zero otherwise. Similarly,  $D_3$  is equal to one in regime three (i.e. in rising mergers activity periods at the beginning of a merger wave), otherwise  $D_3$  equal to zero. The second regime (“normal” merger activity) is captured implicitly by the constant. The use of a third dummy variable would result to perfect collinearity).

If  $\gamma_1$  and  $\gamma_3$  are significantly different from zero the relationship between mergers and acquisitions activity and the Stock Market Index is different under the three different regimes identified in the previous section, for each one of the industrial sectors. In the same path if  $\kappa_1$  and  $\kappa_3$  are significantly different from zero the relationship between mergers and acquisitions activity and the UK Business Cycle Coincident Index is different under the three different regimes. Alternatively, if the estimates of the above coefficient are insignificantly different from zero the relationship between Mergers and Acquisitions activity, the Stock Market and the Business Cycle is the same throughout the three regimes.

The results in Table 4.4.1 provide consistent evidence for the relationship between Mergers and Acquisitions activity, the Stock Market and the Business Cycle. For the overall period (1986:1 through 2005:4) the relationship is reliably nonexistent, for all the industrial sectors, therefore we can conclude that it seems not exist a relationship between the mergers and acquisitions activity, the stock market and the business cycle, at industrial level. At this point it is necessary to note that the

empirical results of this section are contradictory with the results presented in the previous chapter, where a strong positive relationship between the aggregate merger and acquisition activity, the stock market and the business cycle has been identified. The above described contradiction aggregate and industrial sector is quite surprising and lacks strong theoretical and / or empirical explanation. However, Resende (1999) states that the aggregate data definitions have been more consistent over time, making possible the consideration of a longer time series. His observation applies in this case as far as data for M&As at industrial level are not available before 1986. Aggregate data are available since 1969. The latter provides partial explanation for the observed difference in empirical results.

**Table 4.4.1: Relationship between the mergers activity, the stock market and the business cycle (t-values in the parenthesis)**

	<i>FTSE-ALL SHARES</i>	<i>UKCI</i>
<i>Consumer Products and Services</i>	-0.485899 (-1.707588)	0.156438 (0.049892)
<i>Financial Companies</i>	0.234352 (0.887825)	4.046295 (1.144450)
<i>Healthcare</i>	0.238813 (0.253343)	5.462647 (0.757160)
<i>Industrials</i>	0.003656 (0.011886)	1.815688 (0.803838)
<i>Basic Materials</i>	-0.104462 (-0.352704)	6.365317 (1.259094)
<i>Media and Entertainment</i>	0.094769 (0.282086)	1.740001 (0.318477)
<i>Retailers</i>	0.381209 (1.485499)	3.089563 (0.817863)
<i>High Technology</i>	0.235599 (1.355760)	6.039142 (0.970166)
<i>Telecommunications</i>	-0.260528 (-0.610837)	-3.870006 (-0.570199)
<i>Oil and Gas</i>	-0.502496 (-0.889228)	5.366923 (0.448641)

#### **4.4 Summary and Conclusions**

The main aim of this chapter is to investigate the behaviour of mergers and acquisitions in the UK, at industrial level, making use of the Markov switching

models with no autoregressive dynamics and constant transition probabilities, along the lines of chapter 3. A serious obstacle of relevant studies in the area of mergers and acquisitions refers to the necessity of relatively long time series data; typically, empirical studies for the USA have concatenated series produced by a variety of different institutions, despite the caveats that have been made on that type of procedure. The focus of the chapter is on the UK case, for which we consider the longest consistent series available. Quarterly disaggregated data by sector of acquiring firm is used; specifically, we consider the numbers of mergers and acquisitions of independent companies by industrial and commercial companies at sectoral level. Sector classification changes limited our sample to 1986:1 – 2005:4. Moreover, sectors where merger and acquisition activity were virtually nonexistent, such as the tobacco industry, were not considered. The period under investigation is quite representative for the purpose this survey, as far as, according to the Institute of National Statistics from 1986 onwards the British economy is believed to have gone through two full business cycles.

Moreover, chapter 4 aims to examine the relationship between merger and acquisition activity in the UK with the Stock Market and the aggregate economic activity (Business Cycle) at sectoral level, in an attempt to identify forces driving the market for corporate control.

The evidence presented in this chapter suggests that most of the industrial merger and acquisition series display wave characterising autoregressive dynamics.

However, in some industrial sectors a single regime identified - the one of normal merger activity. Moreover, the empirical results suggest that a relationship between the merger and acquisition activity in the UK with the Stock Market and the aggregate economic activity (Business Cycle) at sectoral level does not exist, although in chapter 3 a strong positive one has been identified at aggregate level. In other words, the hypothesis that the aggregate economic activity and the stock market drive the market for corporate control has not been confirmed. This leads us to further investigate the issue employing alternative theories and empirical applications (chapter 5).



## 4.6 Appendix

### **NEW FTSE / DJ INDUSTRY CLASSIFICATION BENCHMARK (ICB)<sup>1</sup>**

Industry	Super-sector	Sector	Sub-sector	Definition
0001 Oil & Gas	0500 Oil & Gas	0530 Oil & Gas Producers	0533 Exploration & Production	Companies engaged in the exploration for and drilling, production, refining and supply of oil and gas products.
			0537 Integrated Oil & Gas	Integrated oil and gas companies engaged in the exploration for and drilling, production, refining and distribution of oil and gas products.
		0570 Oil Equipment, Services & Distribution	0573 Oil Equipment & Services	Suppliers of equipment and services to oil fields and offshore platforms, such as drilling, exploration, seismic-information services and platform construction.
			0577 Pipelines	Operators of pipelines carrying oil, gas or other forms of fuel. Excludes pipeline operators that derive the majority of their revenues from direct sales to end users, which are classified under Gas Distribution.
1000 Basic Materials	1300 Chemicals	1350 Chemicals	1353 Commodity Chemicals	Producers and distributors of simple chemical products that are primarily used to formulate more complex chemicals or products, including plastics and rubber in their raw form, fiberglass and synthetic fibers.
			1357 Specialty Chemicals	Producers and distributors of finished chemicals for industries or end users, including dyes, cellular polymers, coatings, special plastics and other chemicals for specialized applications. Includes makers of colorings, flavors and fragrances, fertilizers, pesticides, chemicals used to make drugs, paint in its pigment form and glass in its

<sup>1</sup> The Industry Classification Benchmark (ICB) structure and codes document, which included in this appendix downloaded from [ftse.co.uk](http://ftse.co.uk).

1700 Basic Resources	1730 Forestry & Paper		unfinished form. Excludes producers of paint and glass products used for construction, which are classified under Building Materials & Fixtures.
		1733 Forestry	Owners and operators of timber tracts, forest tree nurseries and sawmills. Excludes providers of finished wood products such as wooden beams, which are classified under Building Materials & Fixtures.
		1737 Paper	Producers, converters, merchants and distributors of all grades of paper. Excludes makers of printed forms, which are classified under Business Support Services, and manufacturers of paper items such as cups and napkins, which are classified under Nondurable Household Products.
	1750 Industrial Metals	1753 Aluminum	Companies that mine or process bauxite or manufacture and distribute aluminum bars, rods and other products for use by other industries. Excludes manufacturers of finished aluminum products, such as siding, which are categorized according to the type of end product.
		1755 Nonferrous Metals	Producers and traders of metals and primary metal products other than iron, aluminum and steel. Excludes companies that make finished products, which are categorized according to the type of end product.
1770 Mining		1757 Steel	Manufacturers and stockholders of primary iron and steel products such as pipes, wires, sheets and bars, encompassing all processes from smelting in blast furnaces to rolling mills and foundries.
		1771 Coal	Companies engaged in the exploration for or mining of coal.

2000 Industrials	2300 Construction & Materials	2350 Construction & Materials	1773 Diamonds & Gemstones	Companies engaged in the exploration for and production of diamonds and other gemstones.
			1775 General Mining	Companies engaged in the exploration, extraction or refining of minerals not defined elsewhere within the Mining sector.
			1777 Gold Mining	Prospectors for and extractors or refiners of gold-bearing ores.
			1779 Platinum & Precious Metals	Companies engaged in the exploration for and production of platinum, silver and other precious metals not defined elsewhere.
			2353 Building Materials & Fixtures	Producers of materials used in the construction and refurbishment of buildings and structures, including cement and other aggregates, wooden beams and frames, paint, glass, roofing and flooring materials other than carpets. Includes producers of bathroom and kitchen fixtures, plumbing supplies and central air-conditioning and heating equipment. Excludes producers of raw lumber, which are classified under Forestry.
2700 Industrial Goods & Services	2710 Aerospace & Defense	2357 Heavy Construction		Companies engaged in the construction of commercial buildings, infrastructure such as roads and bridges, residential apartment buildings, and providers of services to construction companies, such as architects, masons, plumbers and electrical contractors.
			2713 Aerospace	Manufacturers, assemblers and distributors of aircraft and aircraft parts primarily used in commercial or private air transport. Excludes manufacturers of communications satellites, which are classified under Telecommunications Equipment.
			2717 Defense	Producers of components and equipment for the defense industry, including military aircraft, radar equipment and weapons.

2720 General Industrials	2723 Containers & Packaging	Makers and distributors of cardboard, bags, boxes, cans, drums, bottles and jars and glass used for packaging.
	2727 Diversified Industrials	Industrial companies engaged in three or more classes of business within the Industrial Industry that differ substantially from each other.
2730 Electronic & Electrical Equipment	2733 Electrical Components & Equipment	Makers and distributors of electrical parts for finished products, such as printed circuit boards for radios, televisions and other consumer electronics. Includes makers of cables, wires, ceramics, transistors, electric adapters, fuel cells and security cameras.
	2737 Electronic Equipment	Manufacturers and distributors of electronic products used in different industries. Includes makers of lasers, smart cards, bar scanners, fingerprinting equipment and other electronic factory equipment.
2750 Industrial Engineering	2753 Commercial Vehicles & Trucks	Manufacturers and distributors of commercial vehicles and heavy agricultural and construction machinery, including rail cars, tractors, bulldozers, buses and industrial lawn mowers. Includes nonmilitary shipbuilders, such as builders of cruise ships and ferries.
	2757 Industrial Machinery	Designers, manufacturers, distributors and installers of industrial machinery and factory equipment, such as machine tools, lathes, presses and assembly line equipment. Includes makers of pollution control equipment, castings, pressings, welded shapes, structural steelwork, compressors, pumps, bearings, elevators and escalators.
2770 Industrial Transportation	2771 Delivery Services	Operators of mail and package delivery services for commercial and consumer use. Includes courier and logistic services primarily involving air transportation.

2773 Marine Transportation	Providers of on-water transportation for commercial markets, such as container shipping. Excludes ports, which are classified under Transportation Services, and shipbuilders, which are classified under Commercial Vehicles & Trucks.
2775 Railroads	Providers of industrial railway transportation and railway lines. Excludes passenger railway companies, which are classified under Travel & Tourism, and manufacturers of rail cars, which are classified under Commercial Vehicles & Trucks.
2777 Transportation Services	Companies providing services to the Industrial Transportation sector, including companies that manage airports, train depots, roads, bridges, tunnels, ports, and providers of logistic services to shippers of goods. Includes companies that provide aircraft and vehicle maintenance services.
2779 Trucking	Companies that provide commercial trucking services. Excludes road and tunnel operators, which are classified under Transportation Services, and vehicle rental and taxi companies, which are classified under Travel & Tourism.
2791 Business Support Services	Providers of nonfinancial services to a wide range of industrial enterprises and governments. Includes providers of printing services, management consultants, office cleaning services, and companies that install, service and monitor alarm and security systems.
2793 Business Training & Employment Agencies	Providers of business or management training courses and employment services.
2795 Financial Administration	Providers of computerized transaction processing, data communication and information services, including payroll, bill payment and employee benefit services.
2790 Support Services	

3000 Consumer Goods	3300 Automobiles & Parts	3350 Automobiles & Parts	2797 Industrial Suppliers	Distributors and wholesalers of diversified products and equipment primarily used in the commercial and industrial sectors. Includes builders merchants.
			2799 Waste & Disposal Services	Providers of pollution control and environmental services for the management, recovery and disposal of solid and hazardous waste materials, such as landfills and recycling centers. Excludes manufacturers of industrial air and water filtration equipment, which are classified under Industrial Machinery.
	3300 Automobiles & Parts	3350 Automobiles & Parts	3353 Automobiles	Makers of motorcycles and passenger vehicles, including cars, sport utility vehicles (SUVs) and light trucks. Excludes makers of heavy trucks, which are classified under Commercial Vehicles & Trucks, and makers of recreational vehicles (RVs and ATVs), which are classified under Recreational Products.
			3355 Auto Parts	Manufacturers and distributors of new and replacement parts for motorcycles and automobiles, such as engines, carburetors and batteries. Excludes producers of tires, which are classified under Tires.
			3357 Tires	Manufacturers, distributors and retreaders of automobile, truck and motorcycle tires.
			3533 Brewers	Manufacturers and shippers of cider or malt products such as beer, ale and stout.
	3500 Food & Beverage	3530 Beverages	3535 Distillers & Vintners	Producers, distillers, vintners, blenders and shippers of wine and spirits such as whisky, brandy, rum, gin or liqueurs.
			3537 Soft Drinks	Manufacturers, bottlers and distributors of nonalcoholic beverages, such as soda, fruit juices, tea, coffee and bottled water.
			3573 Farming & Fishing	Companies that grow crops or raise livestock, operate fisheries or own nontobacco plantations. Includes manufacturers of livestock feeds and seeds

3700 Personal & Household Goods	3720 Household Goods		and other agricultural products but excludes manufacturers of fertilizers or pesticides, which are classified under Specialty Chemicals.
		3577 Food Products	Food producers, including meatpacking, snacks, fruits, vegetables, dairy products and frozen seafood. Includes producers of pet food and manufacturers of dietary supplements, vitamins and related items. Excludes producers of fruit juices, tea, coffee, bottled water and other nonalcoholic beverages, which are classified under Soft Drinks.
		3722 Durable Household Products	Manufacturers and distributors of domestic appliances, lighting, hand tools and power tools, hardware, cutlery, tableware, garden equipment, luggage, towels and linens.
		3724 Nondurable Household Products	Producers and distributors of pens, paper goods, batteries, light bulbs, tissues, toilet paper and cleaning products such as soaps and polishes.
	3740 Leisure Goods	3726 Furnishings	Manufacturers and distributors of furniture, including chairs, tables, desks, carpeting, wallpaper and office furniture.
		3728 Home Construction	Constructors of residential homes, including manufacturers of mobile and prefabricated homes intended for use in one place.
		3743 Consumer Electronics	Manufacturers and distributors of consumer electronics, such as TVs, VCRs, DVD players, audio equipment, cable boxes, calculators and camcorders.
		3745 Recreational Products	Manufacturers and distributors of recreational equipment. Includes musical instruments, photographic equipment and supplies, RVs, ATVs and marine recreational vehicles such as yachts, dinghies and speedboats.

4000 Health Care	4500 Health Care	4530 Health Care Equipment & Services	3747 Toys	Manufacturers and distributors of toys and video/computer games, including such toys and games as playing cards, board games, stuffed animals and dolls.
			3763 Clothing & Accessories	Manufacturers and distributors of all types of clothing, jewelry, watches or textiles. Includes sportswear, sunglasses, eyeglass frames, leather clothing and goods, and processors of hides and skins.
			3765 Footwear	Manufacturers and distributors of shoes, boots, sandals, sneakers and other types of footwear.
			3767 Personal Products	Makers and distributors of cosmetics, toiletries and personal-care and hygiene products, including deodorants, soaps, toothpaste, perfumes, diapers, shampoos, razors and feminine-hygiene products. Includes makers of contraceptives other than oral contraceptives, which are classified under Pharmaceuticals.
			3785 Tobacco	Manufacturers and distributors of cigarettes, cigars and other tobacco products. Includes tobacco plantations.
			4533 Health Care Providers	Owners and operators of health maintenance organizations, hospitals, clinics, dentists, opticians, nursing homes, rehabilitation and retirement centers. Excludes veterinary services, which are classified under Specialized Consumer Services.
			4535 Medical Equipment	Manufacturers and distributors of medical devices such as MRI scanners, prosthetics, pacemakers, X-ray machines and other nondisposable medical devices.
			4537 Medical Supplies	Manufacturers and distributors of medical supplies used by health care providers and the general public. Includes makers of contact lenses, eyeglass lenses, bandages and other disposable medical supplies.



5000 Consumer Services	5300 Retail	4570 Pharmaceuticals & Biotechnology	4573 Biotechnology	Companies engaged in research into and development of biological substances for the purposes of drug discovery and diagnostic development, and which derive the majority of their revenue from either the sale or licensing of these drugs and diagnostic tools.
			4577 Pharmaceuticals	Manufacturers of prescription or over-the-counter drugs, such as aspirin, cold remedies and birth control pills. Includes vaccine producers but excludes vitamin producers, which are classified under Food Products.
5000 Consumer Services	5300 Retail	5330 Food & Drug Retailers	5333 Drug Retailers	Operators of pharmacies, including wholesalers and distributors catering to these businesses.
			5337 Food Retailers & Wholesalers	Supermarkets, food-oriented convenience stores and other food retailers and distributors. Includes retailers of dietary supplements and vitamins.
			5371 Apparel Retailers	Retailers and wholesalers specializing mainly in clothing, shoes, jewelry, sunglasses and other accessories.
			5373 Broadline Retailers	Retail outlets and wholesalers offering a wide variety of products including both hard goods and soft goods.
			5375 Home Improvement Retailers	Retailers and wholesalers concentrating on the sale of home improvement products, including garden equipment, carpets, wallpaper, paint, home furniture, blinds and curtains, and building materials.
			5377 Specialized Consumer Services	Providers of consumer services such as auction houses, day-care centers, dry cleaners, schools, consumer rental companies, veterinary clinics, hair salons and providers of funeral, lawn-maintenance, consumer-storage, heating and cooling installation and plumbing services.

5500 Media	5550 Media	5379 Specialty Retailers	Retailers and wholesalers concentrating on a single class of goods, such as electronics, books, automotive parts or closeouts. Includes automobile dealerships, video rental stores, dollar stores, duty-free shops and automotive fuel stations not owned by oil companies.
		5553 Broadcasting & Entertainment	Producers, operators and broadcasters of radio, television, music and filmed entertainment. Excludes movie theaters, which are classified under Recreational Services.
		5555 Media Agencies	Companies providing advertising, public relations and marketing services. Includes billboard providers and telemarketers.
		5557 Publishing	Publishers of information via printed or electronic media.
5700 Travel & Leisure	5750 Travel & Leisure	5751 Airlines	Companies providing primarily passenger air transport. Excludes airports, which are classified under Transportation Services.
		5752 Gambling	Providers of gambling and casino facilities. Includes online casinos, racetracks and the manufacturers of pachinko machines and casino and lottery equipment.
		5753 Hotels	Operators and managers of hotels, motels, lodges, resorts, spas and campgrounds.
		5755 Recreational Services	Providers of leisure facilities and services, including fitness centers, cruise lines, movie theaters and sports teams.
		5757 Restaurants & Bars	Operators of restaurants, fast-food facilities, coffee shops and bars. Includes integrated brewery companies and catering companies.
		5759 Travel & Tourism	Companies providing travel and tourism related services, including travel agents, online travel reservation services, automobile rental firms and companies that primarily provide passenger transportation, such as buses, taxis, passenger rail and

6000 Telecommunications	6500 Telecommunications	6530 Fixed Line Telecommunications	6535 Fixed Line Telecommunications	ferry companies.
		6570 Mobile Telecommunications	6575 Mobile Telecommunications	Providers of fixed-line telephone services, including regional and long-distance. Excludes companies whose primary business is Internet access, which are classified under Internet.
				Providers of mobile telephone services, including cellular, satellite and paging services.
7000 Utilities	7500 Utilities	7530 Electricity	7535 Electricity	Companies generating and distributing electricity, including generation using geothermal, nuclear and solar energy.
		7570 Gas, Water & Multiutilities	7573 Gas Distribution	Distributors of gas to end users. Excludes providers of natural gas as a commodity, which are classified under the Oil & Gas Industry.
			7575 Multiutilities	Utility companies with significant presence in more than one utility.
			7577 Water	Companies providing water to end users, including water treatment plants.
8000 Financials	8300 Banks	8350 Banks	8355 Banks	Banks providing a broad range of financial services, including retail banking, loans and money transmissions.
	8500 Insurance	8530 Nonlife Insurance	8532 Full Line Insurance	Insurance companies with life, health, property & casualty and reinsurance interests, no one of which predominates.
			8534 Insurance Brokers	Insurance brokers and agencies.
			8536 Property & Casualty Insurance	Companies engaged principally in accident, fire, automotive, marine, malpractice and other classes of nonlife insurance.
			8538 Reinsurance	Companies engaged principally in reinsurance.
		8570 Life Insurance	8575 Life Insurance	Companies engaged principally in life and health insurance.

8700 Financial Services	8730 Real Estate	8733 Real Estate Holding & Development	Companies that invest directly or indirectly in real estate through development, management or ownership, including property agencies. Excludes real estate investment trusts and similar entities, which are classified as Real Estate Investment Trusts.
		8737 Real Estate Investment Trusts	Real estate investment trusts or corporations (REITs) and listed property trusts (LPTs.)
		8771 Asset Managers	Companies that provide custodial, trustee and other related fiduciary services. Includes mutual fund management companies.
		8773 Consumer Finance	Credit card companies and providers of personal finance services such as personal loans and check cashing companies.
		8775 Specialty Finance	Companies engaged in financial activities not specified elsewhere. Includes companies not classified under Equity Investment Instruments or Nonequity Investment Instruments engaged primarily in owning stakes in a diversified range of companies.
	8770 General Financial	8777 Investment Services	Companies providing a range of specialized financial services, including securities brokers and dealers, online brokers and security or commodity exchanges.
		8779 Mortgage Finance	Companies that provide mortgages, mortgage insurance and other related services.
		8985 Equity Investment Instruments	Corporate closed-ended investment entities identified under distinguishing legislation, such as investment trusts and venture capital trusts.
		8990 Nonequity Investment Instruments	Noncorporate, open-ended investment instruments such as open-ended investment companies and funds, unit trusts, ETFs, currency funds and split capital trusts.
		8995 Nonequity Investment Instruments	

9000 Technology	9500 Technology	9530 Software & Computer Services	9533 Computer Services	Companies that provide consulting services to other businesses relating to information technology. Includes providers of computer-system design, systems integration, network and systems operations, data management and storage, repair services and technical support.
			9535 Internet	Companies providing internet-related services, such as internet access providers and search engines and providers of Web site design, Web hosting, domain-name registration and e-mail services.
			9537 Software	Publishers and distributors of computer software for home or corporate use. Excludes computer game producers, which are classified under Toys.
		9570 Technology Hardware & Equipment	9572 Computer Hardware	Manufacturers and distributors of computers, servers, mainframes, workstations and other computer hardware and subsystems, such as mass-storage drives, mice, keyboards and printers.
			9574 Electronic Office Equipment	Manufacturers and distributors of electronic office equipment, including photocopiers and fax machines.
			9576 Semiconductors	Producers and distributors of semiconductors and other integrated chips, including other products related to the semiconductor industry, such as semiconductor capital equipment and motherboards. Excludes makers of printed circuit boards, which are classified under Electrical Components & Equipment.
			9578 Telecommunications Equipment	Makers and distributors of high-technology communication products, including satellites, mobile telephones, fiber optics, switching devices, local and wide-area networks, teleconferencing equipment and connectivity devices for computers, including hubs and routers.

## **Chapter 5: Stock Market Driven Mergers and Acquisitions:**

### **Market's versus Manager's Rationality.**

#### ***5.1 Introduction***

A major stream of theoretical and empirical research on mergers and acquisitions reveals that takeover activity comes in waves; this was one of the major research questions in chapters three (aggregate level) and four (industrial level), this thesis dealt with. In this chapter attention will be focused on stock market mis-valuations and their effect on mergers and acquisitions activity. Do stock market mis-valuations drive mergers waves?

The so-called neoclassical theory of takeovers interprets mergers and acquisitions as an efficiency-improving response to various industry shocks, such as antitrust policy or deregulation. In the conglomerate mergers of the 1960s, well-managed bidders built up diversified groups by adding capital and know-how to the target. In the bust-up takeovers of the 1980s, raiders financed by bank debt and junk bonds acquired and split up the very same conglomerates assembled in the 1960s, because this kind of organization was no longer efficient. Finally, the wave of related acquisitions in the 1990s, which still does not have a name, was part consolidation of major industries, and part response to deregulation.

The neoclassical theory of mergers has considerable explanatory power, but it is incomplete. This is mainly because it focuses on industry-specific shocks and it does not explain satisfactorily the aggregate merger waves unless several industries experience shocks at the same time. The theory also does not explain whether cash or stock is used to pay target shareholders, even though there are distinct patterns in the data on means of payment in mergers. On the central prediction of the theory that mergers increase profitability, the evidence is inconclusive. The neoclassical theory is also difficult to reconcile with some stock market evidence as far as recent studies in the area have identified a number of anomalies. More specifically, Loughran and Vijh (1997) found that the market does not react correctly to the news of a merger, with acquirers making cash offers earning positive long-run ARs, and those making stock offers earning negative long-run ARs. Additionally, Rau and Vermaelen (1998) showed that this pattern of returns remains even after the correction for size and B/M ratio, while, Mitchell and Stafford (2000) and Andrade et al (2001) challenged this evidence on the grounds that merger observations are not statistically independent, and present long-run bidder returns that are lower in absolute value and statistically insignificant. Finally, Moeller, Schlingemann, and Stulz (2004) proved empirically that small bidders outperform large bidders.

Recent studies on merger waves [e.g., Maksimovic and Phillips (2001) and Javanovic and Rousseau (2001)] have established a fact that high merger activity is correlated with high stock market valuations. This finding is of particularly

important since high stock market valuations which could sometimes turn out to be mis-valuations may impact merger activities in a systematical way. It is therefore little surprise that recent studies on the wealth effects of mergers have documented a growing body of anomalies, as mentioned above.

In an attempt to accommodate the additional evidence Shleifer and Vishny (2003) and Rhodes-Kropf and Viswanathan (2004) proposed theories of takeovers (*Market timing theory*) related to the neoclassical theory. In this theory, transactions are driven by *stock market valuations* of the merging firms. The fundamental assumption of these models is that financial markets are inefficient, so some firms are valued incorrectly. In contrast, managers are completely rational, understand stock market inefficiencies, and take advantage of them, in part through merger decisions. Mergers in these models are a form of arbitrage by rational managers operating in inefficient markets. According to Shleifer and Vishny (2003), managers rationally respond to less-than-rational markets. The above described theory is in a way the opposite of Roll's (1986) hubris hypothesis of corporate takeovers, in which financial markets are rational, but managers are not.

The main objective of this chapter is to test the undervaluation side of the story within a market / manager rationality framework. Most if not all evidence on the recent debate is drawn exclusively from US data, while merger activities are a universal phenomenon. Therefore, this chapter focuses attention on the other side of the Atlantic for new evidence. A UK sample has been chosen as a representative



sample of European evidence because UK accounts the large majority of European deals [e.g., in Faccio and Masulis (2005), 65.3% of their 13 European country mergers are UK bidders]. Thus the UK sample is particularly interesting under the specific research setting. The rest of chapter is organized as follows: Section two provides a review of the relevant literature; Section three develops the testable hypotheses. Section four describes the data. Section five introduces the methodology used in this empirical study. Section six reports and discusses the empirical findings and finally, section seven concludes the chapter.

## ***5.2 Review of the Literature***

### ***5.2.1 Older Studies in the area – Neoclassical Approach***

In a classic early study, Nelson (1959) used quarterly data on the USA to consider the relationship between merger activity, stock market prices and industrial production over the period 1895-1956. Employing simple regression analysis, he found that there was a positive and significant relationship between merger activity and stock market prices between 1895 and 1920 and, more generally, between 1895 and 1956 whilst he was unable to establish a significant correlation between merger activity and the level of industrial production.

Gort (1969) found concrete links between the economic conditions and the level of acquisitions activity. More specifically, he proposed that acquisitions take place

because the economic conditions change in such a way that the values of the firms were significantly altered.

Later studies have adopted a more sophisticated approach. A good example is the study by Melicher et al. (1983) which analyzed quarterly data on merger activity in the USA in 1947-1977. Using multiple-time-series analysis they found that merger activity was related to both "real" and "capital market" variables in their data. In particular, capital market variables such as stock prices and bond yields tended to "lead" merger activity whilst mergers tended to "lead" changes in industrial activity and business failures.

Other studies have produced mixed results. Geroski (1984) looked at the relationship between mergers and the stock market index in four data sets. Using Granger causality tests he found no "causal" link between mergers and stock prices in his data. He also found that correlations between his variables were unstable. Clark et al. (1988) found evidence of "Granger causality" (in both directions) between stock prices and mergers in US data in 1919-1971. On the other hand, Guerard (1989) found no evidence of "Granger causality" running from stock prices or industrial production to mergers in US data in 1895-1964.

Clarke and Ioannidis (1996) tested the ability of real stock market prices to "Granger cause" merger activity, using two measures of merger activity: the number and the "real" value of mergers. Their empirical results suggested that

stock market returns Granger cause mergers. This relationship holds for the UK from January 1971 to April 1993 when stock prices are measured in real terms and when mergers are measured either by number or real value. The empirical evidence they provided is in contrast with the work done by Geroski (1984) who found no evidence of "causality" and significant evidence of instability in his equations. In their study, real stock market returns were found to be stable predictors of both their measures of merger activity (total number and volume). They also conducted tests for the weak form of stock market efficiency. They found that this was preserved in their model in that lags in stock market returns and mergers could not be used to predict the stock market index.

More recently, Jovanovic and Rousseau (2001, 2002) put forth models under which technological change and subsequent increased dispersion in  $q$  ratios lead to high- $q$  firms taking over low- $q$  firms in waves, while Maksimovic and Phillips (2001) use performance improvements at the plant-level to support a neoclassical theory of merger waves.

Finally, Harford (2005) in his paper presented empirical results that support a neoclassical explanation of merger waves: merger waves occur in response to specific industry shocks that require large scale reallocation of assets. However, according to the author these shocks are not enough on their own. There must be sufficient capital liquidity to accommodate the asset reallocation. The increase in capital liquidity and reduction in financing constraints that is correlated with high

asset values must be present for the shock to propagate a wave. Variables that separately measure capital liquidity and market valuations suggest that the observed relation between high stock market valuations and merger waves has been misattributed to behavioral mis-valuation factors. Rather, the relation is actually driven by the higher capital liquidity (lower transaction costs) that accompanies an economic expansion.

Thus, Harford (2005) offers an intuitive explanation for merger waves: merger waves require both an economic motivation for transactions and relatively low transaction costs to generate a large volume of transactions. The influence of this macro-level liquidity factor causes industry merger waves to cluster in time even if industry shocks do not. The capital liquidity argument modifies the neoclassical hypothesis of waves to predict that only when sufficient capital liquidity exists to accommodate the reallocation of assets, will an industry shock generate a merger wave. Thus, even if industry shocks do not cluster in time, the importance of capital liquidity means that industry merger waves as reactions to shocks will cluster in time to create aggregate merger waves.

To summarize, under the neoclassical hypothesis, once a technological, regulatory, or economic shock to an industry's environment occurs, the collective reaction of firms inside and outside the industry is such that industry assets are reallocated through mergers and partial-firm acquisitions. This activity clusters in time as

managers simultaneously react and then compete for the best combinations of assets.

### ***5.2.2 Market Timing Theory – Behavioral Finance Approach***

The idea that inefficient market mis-valuation is an important driver of the takeover market is not new. For example, Brealey and Myers (2000) discussed a ‘bootstrap’ game, allegedly important during the diversification boom of the 1960’s, based on naïve investor interpretations of price/earnings ratios.

Nevertheless, as discussed by Shleifer and Vishny (2003), the mis-valuation approach to takeovers has had a low profile among academics relative to efficient markets approaches. Shleifer and Vishny (2003) offered a theory in which irrational shifts in investor sentiment affect takeover decisions. In their setting there are no synergies, managers behave rationally, and takeovers are driven purely by irrational stock market mis-valuation.

The misvaluation hypothesis holds that bidders try to profit either by buying undervalued targets for cash at a price below fundamental value; or by paying equity for targets that, even if overvalued, are less overvalued than the bidder. As argued by Shleifer and Vishny (2004), target overvaluation encourages target management to voluntarily accept expropriative offers in order to ‘cash out.’ Bidder and target mis-valuation measures should affect expropriation opportunities

and managerial incentives, and therefore transaction characteristics, including the means of payment (stock versus cash), the form of the offer (merger versus tender offer), the bid premium, hostility of the target to the offer, the success of the bid, and event period returns. The mis-valuation hypothesis also implies that bidders will tend to be overvalued relative to targets, especially among stock offers, in which it is the bidder's relative overvaluation that enables its expropriation of target assets.

The final question answered by the study is why mergers cluster in time. It is not simply that many profitable opportunities for combining firms suddenly become available across a range of industries at a point in time, as a synergy explanation would suggest.

The authors argue that each merger wave of the 1960s, '80s, and '90s was related to market valuation. In the conglomerate wave of the '60s, overvalued firms typically bought less overvalued firms for stock. Mergers in the '60s usually involved firms from different industries. In the hostile takeover waves of the 1980s, when valuations were lower, many acquirers were financiers, and the medium of payment was usually cash. Market undervaluation was central to '80s takeovers, since the absolute valuation of some companies was so low that bidders were willing to use real cash to buy them, borrowing via bank loans or newly issued debt in many cases.

Rising stock market prices in the '90s eliminated the undervaluation of the '80s. The merger wave of the '90s is similar to the '60s, since the medium of payment

was also typically stock, both occurred during periods of very high stock market valuations, and valuations were quite dispersed.

In the same path, Rhodes-Kropf and Viswanathan (2004) proposed a theory, which is based on a rational model of stock mergers and acquisitions. In their model managers of bidding firms have private information about the value of their firms and the potential value of merging with a target firm. Additionally, managers of target firms have private information about the value of their own company. Both bidders and targets have market values that may not reflect the true values of the companies. Furthermore the possible mis-valuations have two components; a firm specific and a market wide component. These can be viewed as mis-priced factors shared by the bidders and targets and mis-priced factors that are not shared. In equilibrium, stock bids reflect the expected level of synergies between the firms engaged in the merger. However, the target firm has limited information about the components of the mis-valuation, and therefore has difficulties to assess the synergies.

The target's managerial team decides whether to accept or reject the offer, based on observing the bidder's fractional offers. The rational managers of the target know whether their own firm is over- or under-valued, but they cannot determine whether this mis-valuation is a market effect, a sector effect or a firm specific effect. Responsibility requires them to accept any offer, which yields more than the stand-alone value. Therefore the decision of the target's managers is based on the assessment of synergies, by the managerial team, given the management's private

information. This assessment of synergies is the critical bid of Rhodes-Kropf and Viswanathan (2004) model.

Since the target's information and the bidder's bid are both positively related to the market wide component of the misevaluation, the target attempts to filter out the market mis-valuation effect. The target form correctly adjusts the bid for potential market over-valuation but puts more weight of the high synergies as well. When the market wide over-valuation is high, the estimation error associated with synergies is high as well, therefore it most likely for the offer to be accepted. Thus, when the market is overvalued, then it is more possible that the target will overestimate the synergies even though the target's managers can see that the price of their firm is also affected by the same overvaluation. This basically happens because the target's managers still underestimates the shared component of the misevaluation.

According to the authors this is because an overvalued target expects that some of this overvaluation is due to a market wide effect and some due to a firm specific effect. Of course the rational target is right on average. However, the more the market is overvalued, the larger is the target's expectation its firm specific mis-valuation because the target management cannot tell which effect is causing their firm's mis-valuation. Therefore the target filters out of the bid just a small portion of the market wide effect when the market is overvalued and too much when the market is undervalued. Therefore the offers tend to look better in a situation of



market overvaluation. The opposite effect occurs when the target is overvalued for firm specific reasons.

In general, if mis-valuation may be related across firms, then the target's assessment of synergies will be positively related to the offer bid but negatively related to the target's real stand alone value. Thus, a target perceives a bid to be high if the synergies are high, the bidding's firm stock is overvalued, or the target is relatively undervalued. Therefore Rhodes-Kropf and Viswanathan (2004) argued that their theory predicts mergers and acquisitions are more likely to occur in undervalued markets or sectors. Additionally, undervalued targets are more likely to accept offers.

Concluding, the theory put forward by Rhodes-Kropf and Viswanathan (2004) demonstrated that merger waves can occur solely because of valuation reasons. However, the authors stressed out that this does not imply that the desire to merge could not be caused by innovation, deregulation or corporate governance issues etc. Rather they suggested that valuation issues impact mergers and acquisitions and merger waves regardless of the underlying motivation for the mergers.

### ***5.2.3 Studies Providing Evidence to the Behavioral Finance Approach***

Ang and Chen (2004), formalized and tested several empirical hypotheses that are inspired by the stock market driven merger theory. Using a sample of more than 3,000 mergers between 1981 and 2001, they found that the probability of a firm

becoming a stock acquirer increases significantly with its degree of overvaluation. They also provided evidence that acquirers are more overvalued in successful stock mergers than in withdrawn mergers. Because overvaluation has to be corrected sooner or later, they compared long-term holding-period returns of the acquirers against a sample of non-acquiring firms that are similarly overvalued. They found that shareholders of stock acquirers, whose overvaluation is greater than their targets' premium-adjusted overvaluation, are better off than similarly overvalued firms that do not make acquisitions. Their results provide evidence that overvaluation could be a motive for most stock acquisitions, although not for all stock mergers.

Dong, Hirshleifer, Richardson and Teoh (2005) proposed an alternative theory, which they called the *Q* hypothesis of takeovers. Their work focuses on how takeover can cause target assets to be employed either more or less efficiently. These changes may derive from elimination of wasteful target behavior, from better bidder investment opportunities, or alternatively from the empire-building propensities of bidders. High market value is an indicator that a firm is 'good,' i.e., is well-run or has good business opportunities, as it reflects the extent to which the firm has succeeded in creating shareholder value from past investment. Takeovers of bad targets by good bidders tend to improve efficiency more than takeovers of good targets by bad bidders. The authors defined mis-valuation as the discrepancy between the current market price and fundamental value. In order to test their hypothesis they employed two contemporaneous proxies for market mis-valuation,

pre-takeover book/price ratios and pre-takeover ratios of residual income model value to price. They argued that mis-valuation of bidders and targets influences the means of payment chosen, the mode of acquisition, the premia paid, target hostility to the offer, the likelihood of offer success, and bidder and target announcement period stock returns. Their empirical evidence was evidence is broadly supportive of the mis-valuation hypothesis.

Rhodes-Kropf, Robinson and Viswanathan (2005) in their paper tested the empirical predictions of Shleifer and Vishny (2003) and Rhodes-Kropf and Viswanathan (2004) and found strong support for the idea that mis-valuation shapes merger activity. They have shown that mis-valuation affects the level of merger activity, the decision to be an acquirer or target, and the transaction medium. In order to guard against the possible alternative interpretations for their empirical findings, they have ruined a battery of empirical horse races between mis-valuation and standard neoclassical explanations of takeover. They argued that even if all spikes in merger activity would attributed to neoclassically motivated industry shocks, their results indicated that mis-valuation is critical for understanding who buys whom in merger transactions. In an attempt to explore mis-valuation empirically, they decomposed Market-to-book value into two parts: Market to book equals Market to value times Value to book. Moreover they provided two alternative interpretations of their results that acquirers have higher firm-specific errors than targets. The first is that mis-valuation matters. Overvalued firms buy less-overvalued firms in sectors that are themselves overvalued.

Alternatively, one could view their decomposition as a refinement of Q theory, in which valuations implied by sector multiples provide better estimates of replacement costs than traditional accounting measures.

Having discussed the two major streams of literature (neoclassical versus behavioral theory of mergers and acquisitions) the hypothesis development, data description, methodology and empirical results of this chapter will follow in the next sections. Table 1 summarizes the predictions of the two approaches.

**Table 5.1: Predictions of the neoclassical and behavioral hypotheses for merger waves<sup>1</sup>**

	Neoclassical	Behavioral
Cause of industry wave	Regulatory or economic shock accompanied by capital liquidity	Overvaluation and dispersion of valuation within industry
Cause of aggregate wave	Multiple simultaneous industry waves clustering because of macro liquidity factor	Overvaluation and dispersion in the aggregate
Cash partial-firm acquisitions	Increase during wave; could be made by stock bidders	Do not increase during wave; are not made by stock bidders

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<sup>1</sup> The table has been obtained from Harford, J. (2005), What Drives Merger Waves?, Journal of Financial Economics, 77 (2005) 529–560.

Pre-wave returns and market-to-book ratios	High if capital liquidity is tied to asset valuation	High
Dispersion in pre-wave returns	No prediction	High
Post-wave returns	No prediction	Low
Measures of tight credit	Low if capital liquidity is important	No prediction
Post-merger operating performance	Better than without a merger	Worse in waves

### ***5.3 Hypothesis Development***

Although a target stock has already had an observable market price, bidders still need to conduct their own valuations of the target. In this process, bidders identify a potential target and make their own valuations. The bid is abandoned (offered) if the valuation is below (above) the target market price<sup>2</sup>. If an offer is made, the difference between the offer price and the pre-announcement market price of the target is called the merger premium.

Given a merger: (1) Under the hubris hypothesis, high merger premium represents a mistake / mis-valuation made by the bidder that may result from excellent pre-bid performance that endows bidder management with both hubris and excess cash. (2) Under the market timing theory, high merger premium represents high deal synergy since bidder management understands the potential value of merging and thus creates value through buying undervalued targets. Indeed, Dong et al., (2005) find targets with lower valuations on average receive higher merger premium. Based on above, two hypotheses are developed as below.

*Hypothesis 1 – Hubris: Irrational managers, rational markets.*

The higher the merger premium paid to the target, the severe the bidder management overconfidence / overpayment, and therefore the worse the market reaction to the merger announcement.

*Hypothesis 2 – Market timing: Rational managers, irrational markets.*

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<sup>2</sup> Because the bidder understands that the target shareholders will not sell their shares to the bidder below the current market price, therefore when the bidder's valuation turn out to be less than target market price no offer will be made.

The higher the merger premium paid to the target, the larger the target's undervaluation or the greater the deal synergy, and therefore the better market reaction to the merger announcement.

Of course, there are two more situations not described by above hypotheses. First, it is possible that both managers and markets are rational. However, if both are rational, we should not expect to observe the anomalies associated with merger performance since in this framework rational managers make correct merger decisions in an efficient market. Second, it may be possible that both managers and markets are irrational. Thus, mergers become random decisions made by irrational managers in an inefficient market. Given the nature of randomness, some deals create value while others destroy value. In an aggregate level, there should be no real gains or losses and no systematic patterns in stock returns of merging firms. Indeed, this situation is unlikely to be true given the fact that mergers are in waves and always clustering in industries, they are by no means random activities. Thus, the above two situations are less likely comparing to the situations proposed under our hypotheses.

It is therefore essential to rethink merger activity under the new framework of market / manager *rationality*. Since empirical evidence show that markets and managers are unlikely to be simultaneously both rational or both irrational, merger activities could thus be mainly driven by the irrationality of either party. Does the



stock market or does the manager's irrationality drive acquisitions? This proposition is tested in the following sections.

#### ***5.4 Sample Data Description***

In this chapter a UK sample of successful public mergers and acquisitions occurring between 1986 and 2005<sup>3</sup> is examined. The sample is drawn from the Securities Data Corporation (SDC) merger and acquisition database based on the following criteria: (1) All bidders are UK public firms, and target firms are UK or international public firms; (2) Financial and utilities firms are excluded; (3) For the purpose of this study, we require that the one-month merger premium data<sup>4</sup> is either directly available from the SDC or can be calculated from the information provided by the SDC. (4) All firms that meet above criteria must have stock prices, size (market value), and book-to-market ratios available from Thomson Financial DataStream. Finally, 470 bidders meet all above mentioned criteria for the period 1986-2004.

Table 2 presents descriptive statistics for the sample. Column 2 reports the number of mergers that occurred in each calendar year. It is evident that the UK acquisition

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<sup>3</sup> Prior to 1985, there is few data available from the Securities Data Corporation (SDC) database for UK public mergers and acquisitions.

<sup>4</sup> Evidence has shown that the most significant market value changes for target firms occur at the merger announcement date or on the day before the announcement. Thus the use of one-month merger premiums should capture the difference between the offer price and the target's pre-merger price. See, for example, Dodd (1980), Asquith (1983), Dennis and McConnell (1986), Huang and Walkling (1987), and Bradley and Jarrell (1988). The one-month merger premium equals the difference between the initial bid price and the target market price four weeks prior to the initial merger announcement divided by the same target price four weeks prior to the announcement.

market experienced a boom in the late 1980s, slowed down between 1990 and 1996 and experienced another boom between 1997 and 2001. The sample is thus representative of the transactions which occurred during the UK merger waves of the late 1980s and 1990s. Column 3 provides the mean and median one-month merger premiums paid for sample targets. Average premiums each year range from 16.76% to 51.05% for the whole sample period. Column 4 shows the mean and median deal values. Average deal value range from 36.2 million to 660.69 million pounds each year. The bidders' mean and median market values each year are reported in Column 5. As can be seen, bidders are much larger than the targets they buy. Column 6 shows mean and median book-to-market ratios of bidders average ranging from 0.05 to 0.60. Moreover, Columns 7 and 8 shows that on average 52% deals are diversifying mergers<sup>5</sup> and 74% are domestic mergers. Finally, Columns 9, 10 and 11 report that on average and through out the sample period 51% of the mergers and acquisitions deals are financed by cash, 24% by stock and 25% by both cash and stock or by alternative means of payment.

## ***5.5 Methodology***

### ***5.5.1 Short-Run Event Studies***

Event studies, introduced by Fama et al. (1969), produce useful evidence on how stock prices respond to information. Many studies focus on returns in a short

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<sup>5</sup> Diversifying deals are mergers that acquirer and target firms do not have the same two-digit SIC code. This is consistent with Megginson, Morgan and Nail (2004), Desai and Jain (1999) and Daley, Mehrotra and Sivakumar (1997).

window (a few days) around a dated event. An advantage of this approach is that because daily expected returns are close to zero, the results are typically insensitive to the model chosen for expected returns and therefore the model does not have a big effect on inferences about abnormal returns. Hence, in the short-run, different event study methodologies provide approximately consistent abnormal returns. Andrade, Mitchell and Stafford (2000) refer to short window event studies as: “The most statistically reliable evidence on whether mergers create value for shareholders”. To an extent, the finance literature provides also evidence that, in the short-run, the choice of benchmark used is not so important (in contrast to long-run studies) for the measurement of abnormal returns.

Event study analysis provides a direct measure of value created for investors and a forward-looking measure of value creation. In theory, stock prices are the present value of expected future cash flows. However, this requires significant assumptions<sup>6</sup> about the functioning of stock markets: efficiency, rationality, and absence of restrictions on arbitrage. Research suggests that for most stocks these are not unreasonable assumptions, on average and over time.

A substantial amount of evidence can be assembled supporting the market efficiency argument. If markets were not efficient they would adjust slowly (or not at all) to new information. Results from over 100 studies carefully documented by Elton and Gruber (1995) show that the market responds rapidly to new

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<sup>6</sup> The basic assumption in studies that focus on short return windows is that any lag in the response of prices to an event is short-lived.

information. In fact, the typical result in event studies using daily data (as in this chapter) is that, on average, stock prices seem to adjust within a day to event announcements. As Jensen (1988) noted, “although the evidence is not literally 100 percent in support of the efficient market hypothesis, no proposition in any of the sciences is better documented”. Thus, there is ample evidence for the market efficiency assumption underlying event study methodology.

### 5.5.2 *The Analysis Approach in This Chapter*

For the purpose of this, the simple Brown and Warner’s (1985) standard event study methodology is adopted. Specifically, Cumulative Average Returns (CARs) for the three-day  $[-1,+1]$  and the five-day  $[-2, +2]$ <sup>7</sup> periods around the announcement date, supplied by Securities Data Corporation (SDC), are calculated.  $R_{i,t}$  is defined as the percentage change of the return for acquiring firm’s security  $i$  at day  $t$ . Therefore,  $AR_{i,t}$  represents the abnormal return for security  $i$  at day  $t$ . In order to capture the announcement period abnormal return of the acquiring firm’s security  $i$ , the market adjusted return is used. Accordingly, for each firm’s security  $i$ , the day  $t$ ’s abnormal return is computed as:

$$AR_{i,t} = R_{i,t} - R_{m,t} \quad (5.1)$$

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<sup>7</sup> The three-day and five-day periods has been chosen because according to Fuller et al. (2002), a five-day window around the merger announcement given by SDC is wide enough to capture the first mention of a merger every time for a sample of about 500 announcements.

Where:

$AR_{i,t}$  = The abnormal return for security  $i$  in time period  $t$ ;

$R_{i,t}$  = The return for the security  $i$  in time period  $t$ ,  $\left[ \frac{(RI_{i,t} - RI_{i,t-1})}{RI_{i,t-1}} \right]$ ; and

$R_{m,t}$  = The return for the market (the FT-All Share measured as the percentage difference of the Market Index) equally weighted index in time period  $t$ .

Fuller's et al. (2002) simple event study methodology is used to calculate the Cumulative Abnormal Returns (CARs) for the three-day  $[-1,+1]$  and five-day periods  $[t-2, t+2]$  around the announcement date of each acquisition. All daily abnormal returns for the periods  $[t-1, t+1]$  and  $[t-2, t+2]$  are summed up where  $t$  is the announcement date as follows:

$$CAR_t = \sum_{t=-2}^{t=+2} AR_{i,t} \quad (5.2)$$

The final step is to average the CAR in order to get the Cumulative Average Residual or Return, which represents the average total effect of the event across all firms over a specified time interval (5 days in our circumstance).

Alternatively, the market adjusted return method can be thought of as an approximation to the market model

$$R_{i,t} = \alpha_i + \beta_i R_{m,t} + \varepsilon_i \quad (5.3)$$

where  $\alpha_i = 0$  and  $\beta_i = 1$  for all firms. Because  $\alpha_i$  is usually small and the average  $\beta_i$  over all firms is 1, this approximation usually produces acceptable results.

Accordingly, the abnormal returns for the acquiring firms are calculated using the standard market model, where the abnormal return for security  $i$  on day  $t$  ( $AR_{i,t}$ ) is the actual return  $R_{i,t}$  minus the security's expected return,  $\alpha_i + \beta_i R_{m,t}$ :

$$AR_{i,t} = R_{i,t} - (\alpha_i + \beta_i R_{m,t}) \quad (5.4)$$

This study does not estimate market parameters based on a time period before each bid, since for frequent acquirers, there is a high probability that previous takeover attempts would be included in the estimation period, hence making beta estimations less meaningful. Additionally, it has been shown that for short window event studies, weighting the market return by the firm's beta does not significantly improve estimation (Brown and Warner, 1985).

### *Conventional parametric student t-test<sup>8</sup>*

The t-statistics are estimated using the cross-sectional variation of abnormal returns. More specifically, the test statistic of the null hypothesis that the mean CARs is equal to zero for a sample of n firms is as follows:

$$t_{CAR} = \overline{CAR_{it}} / \left( \sigma(CAR_{it}) / \sqrt{n} \right) \quad (5.5)$$

Where  $\overline{CAR_{it}}$  denotes the sample average, and  $\sigma(CAR_{it})$  denotes the cross-sectional sample standard deviations of abnormal returns for the sample of n firms.

## **5.6 Empirical Results**

The next step is to empirically test the hypothesis, developed and presented in section 5.3 of this chapter. Additionally, a number of known firm and deal characteristics are employed, in an attempt to enhance the robustness of the empirical results. A two dimensional sorting method is used in order to control for a variety of variables, namely size of the acquirer, relative size of the bidder to target firm, book-to-market ratio of the acquirer, deal diversification, target origin and mode of payment.

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<sup>8</sup> T-statistics reported in this chapter are all generated using MINITAB Release 13.32 statistical software.

### ***5.6.1 Announcement Period CARs of Bidders***

As mentioned earlier in this chapter, according to Schleifer and Vishny (2003) a number of public firms may be valued incorrectly due to ineffective arbitrage or possible lack of information. An important testimony of the hypothesis this chapter deals with is the immediate reaction of the stock market to a merger or acquisition announcement, since mergers reveals to the market new information regarding the values of the bidder and target firm and synergy of the deal. Assuming that some firms are temporarily mis-valued before the announcement, the market, during the announcement period, will reassess and react on whether it perceives the deal as value-destroying (overpay due to hubris) or value creation (buying undervalued targets by rational managers).

Table 5.3 presents the empirical results for the two event windows under investigation (three-day and five-day windows) of the full sample (470 merger and acquisition deals) and three sub samples sorted by merger premium. The merger premium is defined as the four-week pre-announcement premium. It equals the difference between the initial bid price and the target market price four weeks prior to the initial merger announcement divided by the same target price four weeks prior to the announcement. Acquiring firms are ranked by merger premiums and partitioned into three portfolios according to their rankings. Abnormal returns are calculated based on the market-adjusted returns, as described in section 5.5 of this chapter.



For the whole sample, bidders experience small and insignificant three- and five-days CARs. This finding is consistent with the vast majority of studies in the area, which suggest that bidders break even during the announcement period. According to hubris hypothesis, High premium paying acquirers should experience worse returns than the Low premium ones, while market timing predicts that High premium acquirers should have better performance than the Low ones.

Table 5.3 demonstrates that the 3- and 5-day CARs of Low premium acquirers are negative (-1.348% and -1.6581% respectively) and statistically significant at 5% level. For the High acquirer sub portfolio, both 3- and 5-day CARs are negative (-2.53% and -0.44402% respectively) though statistically insignificant. Finally, the High-Low return differentials are 1.095% and 1.2179% for 3-and 5-day respectively both insignificant at 5% level. This evidence is consistent with the market timing hypothesis that High premium paying bidders outperform their Low premium counterparts, since high premium represents large undervaluation of the target and therefore high deal synergy.

#### ***5.6.2 CARs of Bidders Sorted by Merger Premium and Bidder Size***

The size effect has been widely documented in the finance literature. Banz (1981) and Reinganum (1981) find that small-cap stocks earn higher abnormal returns. Specifically, Banz (1981) examined the relationship between the total market value of the common stock of a firm and its return. The results show that, in the 1936 to 1975 period, the common stock of small firms had, on average, higher risk-

adjusted returns than the common stock of large firms. This result will henceforth be referred to as the 'size effect'. This 'size effect' has been in existence for at least forty years and is evidence that the capital asset pricing model is mis-specified. The size effect is not linear in the market value; the main effect occurs for very small firms, while there is little difference in return between average sized and large firms. It is not known whether size per se is responsible for the effect or whether size is just a proxy for one or more true unknown factors correlated with size.

In the same path, Reinganum (1981) argued that his empirical evidence indicates that the anomalous return behavior of low market value firms is perhaps even more astounding than the *E/P* anomaly. A portfolio of fifty small firms experienced average 'abnormal' returns of nearly fifteen percent per year for at least two years. Indeed, after controlling 'abnormal' returns for an *E/P* effect, a large and persistent market value effect is still detected. However, after controlling abnormal returns for market value effects, one could not detect an independent *E/P* effect. Thus, although an *E/P* anomaly and value anomaly are detected when each variable is considered separately, the two anomalies seem to be related to the same set of factors. Furthermore, these factors appear to be more closely associated with firm size than with *E/P* ratios. The value anomaly largely subsumes any *E/P* effect.

In mergers and acquisitions area, empirical studies after documenting that small firms are good acquirers and large firms are not, examine possible explanations for this size effect, defined as the difference between the abnormal returns of small

acquirers and large acquirers. First, roughly one quarter of the firms acquiring public firms are small whereas half of the firms acquiring private firms are small. If acquiring private firms is more profitable than acquiring public firms, this could explain the size effect. Fuller et al. (2002) proved for a sample of firms that make five or more acquisitions in the 1990s that abnormal returns are higher for firms acquiring private firms or subsidiaries than for firms acquiring public firms. Second, small firms are more likely to pay for acquisitions with cash than with equity. Travlos (1987) and others showed that acquisitions of public firms paid for with equity are accompanied by lower announcement returns. However, Chang (1998) and Fuller et al. (2002) argued that acquisitions of private firms paid for with equity do not have lower announcement returns than private acquisitions paid for with cash. Third, small and large acquirers have different characteristics. The literature has shown that a number of acquiring-firm and deal characteristics are related to announcement returns for public-firm acquisitions. For instance, Lang et al. (1991) and Servaes (1991) showed that high q bidders have higher announcement abnormal returns for tender offer acquisitions and public-firm acquisitions, respectively, and Maloney et al. (1993) found that bidders with higher leverage have higher abnormal returns. Finally, Moeller et al., (2004) demonstrated that small firms earn higher announcement period abnormal returns than do large firms. The announcement return for acquiring-firm shareholders is roughly two percentage points higher for small acquirers irrespective of the form of financing and whether the acquired firm is public or private. The size effect is robust to firm and deal characteristics, and it is not reversed over time.

However, if the results presented in Table 3 are valid, it should not be significantly affected by the size effect. Table 4 reports the results for bidder size and merger premium. For large size bidders, the 3- and 5-day CARs for the High merger premium sub-samples are negative (-0.439% and -0.6252% respectively) and statistically insignificant. Moreover, the CARs for the Low merger premium sub-samples are very small and insignificant. The respective High-Low return differentials are positive for the 3-day window and negative for the 5-day but statistically insignificant. For small size bidders, the CARs are all negative and insignificant, but in the sub sample of small size bidders with Low merger premium, where the results are negative (-1.997%) and statistically significant at 5% level of significance. Therefore, Table 5.4 demonstrates similar patterns as observed in Table 5.3, after controlling for the size of the bidding firm.

### ***5.6.3 CARs of Bidders Sorted by Merger Premium and Relative Size between Target and Bidder***

It is generally argued that the relative size<sup>9</sup> of the target to the bidding firm is one of the most significant factors, among others, that affect the bidding firms' announcement window returns. The reaction of the investors when an acquisition is announced is due to the flow of information within a particular market. In the same path, the abnormal returns generated are expected to be higher the larger the target

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<sup>9</sup> The relative size is defined as the ratio of the transaction value of the deal over the market value of the acquiring firm:  $RS = TV_{Deal} / MV_{Bidder}$ . It is obvious that the larger the TV, the larger the relative size of the target to bidding firm will be.

size and thus the more the original structure of the acquiring firm changes as a result of the acquisition, in the case where the announcement of the acquisition is successful. In this study, however, we measure the effect within a small window around the announcement day. In other words, the abnormal returns of the bidding firms are expected to increase along with the relative size of the target to the acquiring firm.

A variety of studies have been carried out to examine the impact of the relative size of target to bidder on acquiring firms' stock performance. Asquith, Bruner, and Mullins (1983) found that acquirers' abnormal returns depend on their relative size in their attempt to assess the gains accruing to bidding firms' shareholders. The relative size of target and bidding firms is incorporated in the analysis, and the market's reaction to the firms' first four merger bids is explicitly compared. The period before 1969 is also compared to the period after 1969. Their results proved that relative size has significant explanatory power, and that its omission may be partially responsible for the inconclusive findings of earlier studies. Moreover, Ang and Kohers (2001), report that relative size significantly affects bidder's post-merger stock performance. Finally, Fuller, Netter, and Stegemoller (2002) show that the larger the relative size (in the acquisition of public targets), the lower the acquirers' abnormal returns. Specifically, when they partitioned the returns to acquirers on the relative size of the target compared to the bidder, they found that there is a positive relationship between the target's relative size and the acquirer's positive abnormal returns.

Given above evidence, we control both relative size and merger premium in our study. Table 5 summarizes the results. All CARs for the High premium sub samples, for both the event windows under investigation are insignificant at 5% level of significance. Turning attention to the Low premium samples the empirical evidence suggests that CARs are negative for all the sub samples and significant at 5% level of significance for firms with large bidder to target relative size. Finally, the High-Low return differentials are positive but insignificant at 5% level. So, results presented in Table 5.5 do not affect the general patterns as observed in Table 5.3, after controlling for the relative size of the bidding to target firm.

#### ***5.6.4 CARs of Bidders Sorted by Merger Premium and Book-To-Market-Value (BTMV) ratio***

It is generally argued that the Book-to-market value (henceforth BTMV) of the acquiring firm is a major determinant of announcement window abnormal returns, as it reflects important information about the past and hence potential future stock performance of the bidding firms abnormal returns. Accordingly, Rau and Vermaelen (1998), Sudarsanam and Mahate (2003) and Conn et al. (2005) reach the conclusion that value acquirers (i.e. acquirers with low BTMV) outperform glamour ones (i.e. acquirers with high BTMV) after the announcement of the acquisition. Glamour acquirers are those firms that are overvalued on the basis of their past stock market performance. Thus, those stocks receive premium ratings in the form of higher BTMV. In contrast firms with low BTMV ratings are

undervalued, but they may have the potential for subsequent value gains. In other words, glamour acquirers are high growth, while value acquirers are low growth firms, since their high market valuation may reflect the expected high growth or investment opportunities. Therefore, it is expected that the lower BTMV, the higher the abnormal returns of the bidding firms within a small window surrounding the acquisition announcement day.

The performance extrapolation hypothesis (Rau and Vermaelen, 1998) states that investors over-extrapolate the past positive performance of glamour acquirers (characterized as having a low book-to-market ratio) thinking that it can be sustained in the future, while penalizes value acquirers (characterized as having a high book-to-market ratio) also based on the idea that poor recent performance will persist. Thus, bidder status (value or glamour) affects their stock performance. However, if market timing is the main reason for merger activities, then our general results reported in Table 5.3 should not be largely affected by the book-to-market effect.

Table 5.6 reports the results sorted by merger premium and book-to-market ratio. Regarding the three-days window CARs in all the sub samples are negative and insignificant, but in the small book-to-market ratio / Low merger premium sub sample, where CARs are negative (-1.521%) and significant at 5% level of significance. In the five-days window case, CARs in the small book-to-market ratio / Low merger premium sub sample are negative (-1.628%) and significant at 5%

level of significance, while in the small book-to-market ratio / High merger premium sub sample are positive. Finally, the High-Low return differentials are positive but insignificant at 5% level. Therefore, Table 5.6 shows similar patterns as observed in Table 3, after controlling for the book-to-market value ratio of the bidding firm.

#### ***5.6.5 CARs of Bidders Sorted by Merger Premium and Domestic or Cross Border Target***

In our sample, though all bidders are UK public firms, the targets are either UK or international public firms. Thus, some transactions are domestic while others are foreign deals. In general, the literature suggests different market reactions to domestic versus foreign acquisitions. (Doukas and Travlos (1988), Kang (1993), Fatemi and Furtado (1998), Goergen and Renneboog (2004), Conn et al. (2005), and Gregory and McCorriston (2005)). We thus control for both target origin and merger premium in this chapter.

According to the results presented in table 5.7, CARs are negative and significant at 5% significance level for the Low premium / domestic target (-1.325%), and negative and significant at 10% significance level for the Low premium / cross border target (-1.413), in the three-day event window. In the five-day event window CARs are negative and significant at 5% significance for both the Low premium / domestic target (-1.604%) and Low premium / cross border target (-



1.807) sub samples. Finally, CARs are negative and insignificant in the High premium / domestic target sub sample and positive but insignificant in the High premium / cross border target sub sample. Finally, the High-Low return differentials are positive but insignificant at 5% level. Thus, Table 5.7 does not affect significantly the results in Table 3, after controlling for the origin of the target firm.

#### ***5.6.6 CARs of Bidders Sorted by Merger Premium and Focused or Diversified Deal***

Some of the most important reasons for companies to engage into mergers and acquisitions into the same and / or different industries might be their desire to increase the scale and efficiency of their current operations, to increase market power, to enter into a new business area, or to utilize the firm's financial capabilities. In other words, the above mentioned motivations represent the main objectives of any firm to increase its profitability, and therefore the wealth of the shareholders. Accordingly, Porter (1980) found that given the variation of the profitability within different industrial sectors, some sectors appear to offer more attractive opportunities for mergers and acquisitions than others. Indeed, a variety of studies in the area have shown that firms they operate within the profitable industries tend to make more related acquisitions, while those from less profitable sectors turn towards unrelated inter-industry (diversified) acquisitions in an attempt to enhance their profit potential (Christensen and Montgomery, 1981 – among

others). Similarly, Wurgler (2000) indicates that countries with developed financial sectors, increase investments more in their growing industries and decrease investments in their declining industries, compared to those with less developed financial sector. Therefore, it is expected, to some degree, the valuation effect to vary significantly within the domestic market for corporate control with respect to whether or not a deal can be classified as focused (within the same industrial sector), or diversified (across different industrial sectors).

Morck, Shleifer and Vishny (1990) using a sample of 326 US mergers and acquisitions found that the returns to bidding shareholders are lower when the firm acquires a target which operates in a different industry and higher when the target firm operates in the same industrial sector with the bidder. Accordingly, Maquiera, Megginson and Nail (1998) find capital markets react negatively to diversifying mergers. Moreover, Megginson, Morgan and Nail (2004), using a sample selection and benchmarking methodology designed to more accurately assess merger-related changes in corporate focus, found a significantly positive relationship between corporate focus and long-term merger performance. Focus-decreasing (FD) mergers result in significantly negative long-term performance with an average 18% loss in stockholder wealth, 9% loss in firm value, and significant declines in operating cash flows three years after merger. Mergers that either preserve or increase focus (FPI) result in marginal improvements in long-term performance. A positive relationship between changes in focus and long-term performance continues to hold after controlling for other variables.

In contrast to the above mentioned studies, according to the empirical findings of Agrawal, Jaffe and Mandelker (1992) diversifying deals earn higher post-merger stock returns, than mergers and acquisitions within the same industry. Thus, diversification is an important factor that should be controlled when measuring merger performance. At this point it should be noted that this chapter identifies as focused all mergers and acquisitions where the bidding and target firms have the same two-digit standard industrial classification (SIC) code as the sample firm. The use of the two-digit SIC code is consistent with Megginson, Morgan and Nail (2004), Desai and Jain (1999), and Daley et al. (1997).

Table 5.8 presents results sorted by both diversification and merger premium. Once again, negative CARs for all Low premium sub-samples are observed with CARs for focused mergers sub samples to be significant at 5% level of significance are observed. CARs for High premium sub-samples are positive in the focused mergers sub sample for the three-day window and negative and insignificant in the remaining cases. Finally, the High-Low returns differentials insignificant at 5% level, but in the case of focused mergers, where CARs found to be positive and significant at 5% level of significance for the three-day window. Therefore, Table 5.8 demonstrates similar patterns as observed in Table 5.3, after controlling for diversification of the deal.

#### ***5.6.7 CARs of Bidders Sorted by Merger Premium and Mode of Payment***

Travlos (1987) and others show that acquisitions of public firms paid for with equity are accompanied by lower announcement returns. However, Chang (1998) and Fuller et al. (2002) found that when mergers and acquisitions are partitioned on method of payment (cash, stock or combination of the two) acquisitions of public targets result in insignificant returns for cash or combination offers but significantly negative returns to acquirers when stock is offered. However for private and subsidiary targets, acquirer returns found to be significantly positive regardless of the method of payment. These acquirer returns accompanying bids for private and subsidiary firms are greater for bids financed with equity than for acquisitions paid with cash.

Results for CARs of Bidders Sorted by Merger Premium and Mode of Payment are presented in table 5.9. 'Cash' includes transactions conducted solely by cash. Stock offers are defined as transactions made solely by common stock. 'Mixed/Other' includes all other transactions financed with both cash and stock and/or methods classified as "other" by Security Data Corporation (SDC). CARs for Low merger premium sub samples are found to be negative but insignificant when the merger is finance by cash for both the event windows under investigation (-0.2% and -0.515% respectively), negative and significant at 10% level of significance when the merger is finance by stock for both the event windows under investigation (-3.35 % and -3.66% respectively) and negative and significant at 5% level of

significance when the merger is finance by both cash and stock or alternatively for both the event windows under investigation (-1.862 % and -2.159% respectively). In the High merger premium sub samples CARs are insignificant in all cases. Finally, the High-Low returns differentials insignificant at 5% level. Therefore, Table 5.9 does not affect the observations for the general results presented in Table 5.3, after controlling for the deal's mode of payment.

Concluding, the after controlling for all the above firm and deal characteristics the empirical results of this chapter remain consistent with the market timing theory. In other words the second hypothesis of section 5.3, which suggests that the higher the merger premium paid to the target, the larger the target's undervaluation or the greater the deal synergy, and therefore the better market reaction to the merger announcement (*rational managers, irrational markets*) seems to be confirmed.

### ***5.7 Concluding Remarks***

Recent explanations of merger waves as the outcome of attempts to time market mis-valuations have refocused the literature on an old question: what causes merger waves? In this chapter, the two main strands in the area are examined: the neoclassical model, in which industries responding to shocks reorganize through mergers and acquisitions, and thereby create a clustering of merger activity; versus, the behavioral model, in which rational managers take advantage of consistent pricing errors in the market to buy real assets with overvalued stock.

The tests in this chapter directly compare the two explanations and support the behavioral model. The empirical evidence suggests that stock market reactions to merger announcements in short-run are consistent with the market timing theory of mergers. Taking together, the results of this chapter provide strong support to the proposition that stock market mis-valuation and the market timing ability of manager is the main driving forces behind merger activities. They also add evidence to the growing field of behavioral corporate finance that suggest that managerial decisions are primarily driven by mis-valuation of financial markets and the managers' desire to time the market.

The fundamental assumption of the model is that financial markets are inefficient, so some firms are valued incorrectly. In contrast, managers are completely rational, understand stock market inefficiencies, and take advantage of them, in part through merger decisions. Mergers in this model are a form of arbitrage by rational managers operating in inefficient markets. As Shleifer and Vishny (2003) pointed out "the model points to a powerful incentive for firms to get their equity overvalued, so that they can make acquisitions with stock. In a more general framework, firms with overvalued equity might be able to make acquisitions, survive, and grow, while firms with undervalued, or relatively less overvalued, equity become takeover targets themselves. The benefit of having a high valuation for making acquisitions also points to an incentive to raise a firm's stock price even through earnings manipulation, a phenomenon whose prevalence is becoming increasingly apparent" (Shleifer and Vishny, 2003, p. 309).

**Table 5.2. Descriptive statistics for mergers deals between 1986-2005**

The sample consists of 470 U.K. public bidders that have acquired one or more public UK of international target firms between the years 1986 and 2005. The merger premium is defined as the four-week pre-announcement premium. It equals the difference between the initial bid price and the target market price four weeks prior to the initial merger announcement divided by the same target price four weeks prior to the announcement. The deal value (£million) is the total value of consideration paid by the acquirer, excluding fees and expenses. Bidder size is the market capitalization of acquirers at the time of merger announcement. Bidder book-to-market ratio is the book value of equity divided by the market capitalization at the time of merger announcement. Diversifying is the percentage of diversifying merger deals. A deal is classified as diversifying when the acquirer takes over a target with a different two-digit SIC industry code. Domestic is the percentage of domestic merger deals. The median values are shown in parentheses.

Year	Number of Firms	Premium (%)	Deal Value (£m)	Bidder Size (£m)	Bidder B/M	Diversifying (%)	Domestic (%)	Financed with Cash (%)	Financed with Stock (%)	Financed with Cash & Stock or Other (%)
1986	5	44.53 (43.29)	673.43 (308.00)	1319.9 (342.6)	0.36 (0.58)	60	0	0	40	60
1987	22	27.75 (30.36)	95.46 (40.09)	882 (326.7)	0.40 (0.45)	64	68	46	36	18
1988	29	51.05 (45.27)	306.58 (73.46)	632.6 (151)	0.49 (0.59)	62	66	76	10	14
1989	26	35.98 (39.62)	66.77 (23.26)	286.6 (112.5)	0.48 (0.57)	62	73	54	27	19
1990	14	49.43 (47.83)	177.58 (42.41)	1341 (326.9)	0.35 (0.39)	79	57	71	0	29
1991	22	29.81 (33.77)	93.58 (19.51)	621.5 (156.4)	0.60 (0.77)	73	91	36	32	32
1992	12	16.76 (16.24)	83.72 (22.43)	398.4 (203.5)	0.38 (0.39)	92	92	51	17	42

1993	12	46.55 (46.42)	36.20 (14.04)	600.5 (217.1)	0.48 (0.52)	75	83	51	17	42
1994	10	31.24 (39.69)	44.90 (37.98)	212 (125.92)	0.07 (0.43)	90	90	60	30	10
1995	19	36.28 (37.40)	166.94 (35.17)	1454.6 (653.3)	0.31 (0.40)	53	74	47	21	32
1996	11	31.85 (31.74)	89.30 (55.40)	705 (440.3)	0.05 (0.29)	55	82	64	9	27
1997	22	49.55 (44.58)	613.52 (37.21)	1442.3 (319.4)	0.20 (0.36)	55	82	41	41	18
1998	40	43.98 (45.07)	182.44 (72.06)	1021.2 (232.4)	0.30 (0.50)	45	80	47	30	23
1999	54	50.48 (38.03)	341.52 (64.32)	1758.5 (212.5)	0.25 (0.58)	54	81	41	24	35
2000	46	46.19 (45.74)	660.69 (116.63)	6557.5 (464.7)	0.21 (0.54)	37	72	46	28	26
2001	28	34.22 (26.46)	214.41 (52.87)	6546.8 (2072.6)	0.21 (0.67)	32	57	61	18	21
2002	17	30.40 (24.19)	369.52 (42.92)	3664.5 (1842.1)	0.33 (0.50)	12	59	70	18	12
2003	28	26.74 (21.21)	285.44 (66.68)	11154.1 (1057.4)	0.47 (0.65)	21	54	50	21	29
2004	28	9.94 (17.36)	139.14 (56.86)	3555.4 (592.3)	0.36 (0.45)	57	75	61	21	18
2005	25	14.54 (18.25)	211.56 (101.96)	1838.1 (189.5)	0.36 (0.40)	36	76	44	28	28
Total	470	36.75 (35.3)	267.7 (48.06)	2749.8 (313.5)	0.26 (0.51)	52	74	51	24	25



**Table 5.3. Announcement Period CARs of Bidders**

The sample consists of 470 U.K. public bidders that have acquired one or more public UK of international target firms between the years 1986 and 2005. The merger premium is defined as the four-week pre-announcement premium. It equals the difference between the initial bid price and the target market price four weeks prior to the initial merger announcement divided by the same target price four weeks prior to the announcement. Acquiring firms are ranked by merger premiums and partitioned into three portfolios according to their rankings. Abnormal returns are calculated based on the market-adjusted returns:

$$AR_i = R_i - R_m$$

Where,  $R_i$  is the return on event firm  $i$  and  $R_m$  is the value-weighted market index return. T-statistics are reported in square brackets.

<i>Event Window</i>	<i>All Deals</i>	<i>Low Premium Deals</i>	<i>Medium Premium Deals</i>	<i>High Premium Deals</i>	<i>High – Low</i>
(-1,+1)	-0.0626 (-1.94)***	-0.01348 (-2.52)**	-0.0273 (-0.46)	-0.0253 (-0.46)	0.01095 (1.43)
(-2,+2)	-0.0693 (-1.94)***	-0.016581 (-2.76)**	0.000228 (-0.04)	-0.004402 (-0.75)	0.012179 (1.45)

- \* Denotes significance at the 1% level.
- \*\* Denotes significance at the 5% level.
- \*\*\* Denotes significance at the 10% level.

**Table 5.4. CARs of Bidders Sorted by Merger Premium and Bidder Size**

The sample consists of 470 U.K. public bidders that have acquired one or more public UK of international target firms between the years 1986 and 2005. The merger premium is defined as the four-week pre-announcement premium. It equals the difference between the initial bid price and the target market price four weeks prior to the initial merger announcement divided by the same target price four weeks prior to the announcement. Acquiring firms are ranked by merger premiums and partitioned into three portfolios according to their rankings. Additionally, they are divided into two sub-groups with respect to the Bidder Size (Market Value). MV is the market value of the acquirer one month prior to the acquisition as provided by DataStream . Abnormal returns are calculated based on the market-adjusted returns:

$$AR_i = R_i - R_m$$

Where,  $R_i$  is the return on event firm  $i$  and  $R_m$  is the value-weighted market index return. T-statistics are reported in square brackets.

<i>Event Window</i>	<i>Low Premium Deals</i>	<i>Medium Premium Deals</i>	<i>High Premium Deals</i>	<i>High – Low</i>
(-1,+1)				
<i>Small</i>	-0.01997 (-2.36)**	-0.00874 (-1.14)	-0.00070 (-0.08)	0.0193 (1.59)
<i>Large</i>	-0.00657 (-1.03)	0.00284 (0.34)	-0.00439 (-0.65)	0.00218 (0.23)
(-2,+2)				
<i>Small</i>	-0.027499 (0.004)	-0.004777 (0.599)	-0.002577 (0.771)	0.0254 (1.98)***
<i>Large</i>	-0.004945 (0.507)	0.004862 (0.593)	-0.006252 (0.424)	-0.0059 (-0.56)

- \* Denotes significance at the 1% level.
- \*\* Denotes significance at the 5% level.
- \*\*\* Denotes significance at the 10% level.

**Table 5.5. CARs of Bidders Sorted by Merger Premium and Relative Size between Target and Bidder**

The sample consists of 470 U.K. public bidders that have acquired one or more public UK of international target firms between the years 1986 and 2005. The merger premium is defined as the four-week pre-announcement premium. It equals the difference between the initial bid price and the target market price four weeks prior to the initial merger announcement divided by the same target price four weeks prior to the announcement. Acquiring firms are ranked by merger premiums and partitioned into three portfolios according to their rankings. Additionally, they are divided into two sub-groups with respect to the Relative Size of Bidder and Target. Relative size is the transaction value divided by the acquirer market value (TV/MV). The transaction value (TV) is from Security Data Corporation (SDC) and represents the total value paid by the acquirer for each bid. MV is the market value of the acquirer one month prior to the acquisition, as provided by DataStream. Abnormal returns are calculated based on the market-adjusted returns:

$$AR_i = R_i - R_m$$

Where,  $R_i$  is the return on event firm  $i$  and  $R_m$  is the value-weighted market index return. T-statistics are reported in square brackets.

<i>Event Window</i>	<i>Low Premium Deals</i>	<i>Medium Premium Deals</i>	<i>High Premium Deals</i>	<i>High – Low</i>
(-1,+1)				
<i>Small</i>	-0.00265 (-0.44)	0.00406 (0.53)	-0.00214 (-0.37)	0.00051 (0.06)
<i>Large</i>	-0.02220 (-2.68)**	-0.00758 (-0.93)	-0.0032 (-0.29)	0.0190 (1.36)
(-2,+2)				
<i>Small</i>	-0.00400 (-0.55)	0.01040 (1.15)	-0.00047 (-0.07)	0.00353 (0.35)
<i>Large</i>	-0.02738 (-2.99)**	-0.00678 (-0.76)	-0.0103 (-0.95)	0.0171 (1.21)

- \* Denotes significance at the 1% level.
- \*\* Denotes significance at the 5% level.
- \*\*\* Denotes significance at the 10% level.

**Table 5.6. CARs of Bidders Sorted by Merger Premium and Book-To-Market-Value (BTMV) ratio**

The sample consists of 470 U.K. public bidders that have acquired one or more public UK of international target firms between the years 1986 and 2005. The merger premium is defined as the four-week pre-announcement premium. It equals the difference between the initial bid price and the target market price four weeks prior to the initial merger announcement divided by the same target price four weeks prior to the announcement. Acquiring firms are ranked by merger premiums and partitioned into three portfolios according to their rankings. Additionally, they are divided into two sub-groups with respect to the Bidder's BTMV ratio. BTMV represents the book-To-market value of equity one month prior to the acquisition as provided by DataStream. Abnormal returns are calculated based on the market-adjusted returns:

$$AR_i = R_i - R_m$$

Where,  $R_i$  is the return on event firm  $i$  and  $R_m$  is the value-weighted market index return. T-statistics are reported in square brackets.

<i>Event Window</i>	<i>Low Premium Deals</i>	<i>Medium Premium Deals</i>	<i>High Premium Deals</i>	<i>High – Low</i>
<i>(-1,+1)</i>				
<i>Small</i>	-0.01521 (-2.01)**	0.00422 (0.50)	-0.00140 (-0.19)	0.0138 (1.30)
<i>Large</i>	-0.01169 (-1.53)	-0.00933 (-1.20)	-0.00369 (-0.45)	0.0080 (0.72)
<i>(-2,+2)</i>				
<i>Small</i>	-0.01628 (-2.02)**	0.00347 (0.35)	0.00041 (0.05)	0.0167 (1.48)
<i>Large</i>	-0.01689 (-1.88)***	-0.00285 (-0.35)	-0.00928 (-1.06)	0.0076 (0.61)

\* Denotes significance at the 1% level.

\*\* Denotes significance at the 5% level.

\*\*\* Denotes significance at the 10% level.

**Table 5.7. CARs of Bidders Sorted by Merger Premium and Domestic or Cross Border Target**

The sample consists of 470 U.K. public bidders that have acquired one or more public UK of international target firms between the years 1986 and 2005. The merger premium is defined as the four-week pre-announcement premium. It equals the difference between the initial bid price and the target market price four weeks prior to the initial merger announcement divided by the same target price four weeks prior to the announcement. Acquiring firms are ranked by merger premiums and partitioned into three portfolios according to their rankings. Additionally, they are divided into two sub-groups with respect to the origin of the target company (domestic or cross border). Abnormal returns are calculated based on the market-adjusted returns:

$$AR_i = R_i - R_m$$

Where,  $R_i$  is the return on event firm  $i$  and  $R_m$  is the value-weighted market index return. T-statistics are reported in square brackets.

<i>Event Window</i>	<i>Low Premium Deals</i>	<i>Medium Premium Deals</i>	<i>High Premium Deals</i>	<i>High – Low</i>
<i>(-1,+1)</i>				
<i>Domestic</i>	-0.01325 (-1.96) **	-0.00524 (-0.82)	-0.00285 (-0.41)	0.01040 (1.07)
<i>Cross Border</i>	-0.01413 (-1.87) ***	0.0051 (0.40)	-0.00171 (-0.21)	0.0124 (1.13)
<i>(-2,+2)</i>				
<i>Domestic</i>	-0.01604 (-2.11) **	0.00391 (-0.55)	-0.00688 (-0.94)	0.0092 (0.87)
<i>Cross Border</i>	-0.01807 (-2.12) **	0.0131 (0.92)	0.00217 (0.24)	0.0202 (1.61)

- \* Denotes significance at the 1% level.
- \*\* Denotes significance at the 5% level.
- \*\*\* Denotes significance at the 10% level.

**Table 5.8. CARs of Bidders Sorted by Merger Premium and Focused or Diversified Deal**

The sample consists of 470 U.K. public bidders that have acquired one or more public UK of international target firms between the years 1986 and 2005. The merger premium is defined as the four-week pre-announcement premium. It equals the difference between the initial bid price and the target market price four weeks prior to the initial merger announcement divided by the same target price four weeks prior to the announcement. Acquiring firms are ranked by merger premiums and partitioned into three portfolios according to their rankings. Additionally, the sample in this case is restricted according to the target industry. Acquisitions in the same industry are defined as focused, while acquisitions across different industries are defined as diversified. Abnormal returns are calculated based on the market-adjusted returns:

$$AR_i = R_i - R_m$$

Where,  $R_i$  is the return on event firm  $i$  and  $R_m$  is the value-weighted market index return. T-statistics are reported in square brackets.

<i>Event Window</i>	<i>Low Premium Deals</i>	<i>Medium Premium Deals</i>	<i>High Premium Deals</i>	<i>High – Low</i>
<i>(-1,+1)</i>				
<i>Focused</i>	-0.02640 (-3.07)**	-0.00863 (-1.03)	0.00194 (0.23)	0.0283 (2.36)**
<i>Diversified</i>	-0.00167 (-0.26)	0.00273 (0.35)	-0.00684 (-0.95)	-0.00517 (-0.54)
<i>(-2,+2)</i>				
<i>Focused</i>	-0.03079 (-3.23)**	-0.00453 (-0.50)	-0.00339 (-0.37)	0.0274 (2.09)**
<i>Diversified</i>	-0.00359 (-0.49)	0.00463 (0.51)	-0.00538 (-0.71)	-0.0018 (-0.17)

- \* Denotes significance at the 1% level.
- \*\* Denotes significance at the 5% level.
- \*\*\* Denotes significance at the 10% level.

**Table 5.9. CARs of Bidders Sorted by Merger Premium and Mode of Payment**

The sample consists of 470 U.K. public bidders that have acquired one or more public UK of international target firms between the years 1986 and 2005. The merger premium is defined as the four-week pre-announcement premium. It equals the difference between the initial bid price and the target market price four weeks prior to the initial merger announcement divided by the same target price four weeks prior to the announcement. Acquiring firms are ranked by merger premiums and partitioned into three portfolios according to their rankings. Additionally, they are further divided by the method of payment. 'Cash' includes transactions conducted solely by cash. Stock offers are defined as transactions made solely by common stock. 'Mixed/Other' includes all other transactions financed with both cash and stock and/or methods classified as "other" by Security Data Corporation (SDC). Abnormal returns are calculated based on the market-adjusted returns:

$$AR_i = R_i - R_m$$

Where,  $R_i$  is the return on event firm  $i$  and  $R_m$  is the value-weighted market index return. T-statistics are reported in square brackets.

<i>Event Window</i>	<i>Low Premium Deals</i>	<i>Medium Premium Deals</i>	<i>High Premium Deals</i>	<i>High – Low</i>
(-1,+1)				
<i>Cash</i>	-0.00200 (-0.34)	0.01425 (1.81)***	0.00490 (0.77)	0.00690 (0.79)
<i>Stock</i>	-0.0335 (-1.81)***	-0.0219 (-1.77)***	-0.0054 (-0.40)	0.0280 (1.22)
<i>Mixed / Other</i>	-0.01862 (-2.62)**	-0.0152 (-1.49)	-0.0191 (-1.61)	-0.0005 (-0.03)
(-2,+2)				
<i>Cash</i>	-0.00515 (-0.75)	0.01940 (2.23)**	0.00683 (1.00)	0.01199 (1.24)
<i>Stock</i>	-0.0366 (-1.94)***	-0.0252 (-1.79)***	-0.0160 (-1.11)	0.0206 (0.86)
<i>Mixed / Other</i>	-0.02159 (-2.20)**	-0.0104 (-0.92)	-0.0199 (-1.58)	0.0017 (0.11)

\* Denotes significance at the 1% level.

\*\* Denotes significance at the 5% level.

\*\*\* Denotes significance at the 10% level.

## **Chapter 6: Conclusion and Thoughts for Further Research**

Attempts to formulate a complete theory based on the relationship between merger activity and macroeconomic and / or financial variables has proved to be very difficult and so such attempt, as yet, commands general or even partial acceptance. The latter point motivated this thesis, which aims to contribute to the discussion of mergers and acquisitions activity behavior. More specifically, this thesis attempts to verify that mergers and acquisitions activity is cyclical and driven by the aggregate economic activity and the stock market. At a second stage it moves to examine and empirically test the *Market Timing Theory* of corporate takeovers, as introduced by Shleifer and Vishny (2003) and Rhodes-Kropf and Viswanathan (2004), which lies on the assumptions that mergers waves are driven by stock market mis-valuations.

The thesis contributes to the literature in several ways: (1) It verifies the assumption that mergers and acquisitions come in waves at both aggregate and industrial level, adopting non linear time series models that naturally accommodate the notion of discrete shifts associated with wave behavior. (2) It extends existing research by allowing the series to follow three regimes with different mean values enabling the series to be modeled using multiple time series representations. (3) It provides accurate dating of each mergers wave in the UK at both aggregate and industrial level. (4) It succeeds to identify a significant relationship between the aggregate mergers and acquisitions activity the business cycle and the stock



market. (5) It provides empirical evidence that supports the *Market Timing Theory* of corporate takeovers (Shleifer and Vishny, 2003 and Rhodes-Kropf and Viswanathan, 2004).

More specifically, the empirical evidence in Chapter Three suggests that there exist three distinctly different types of behavior (regimes) in the series of mergers and acquisitions numbers. The results reported suggest, the dominant regime is Regime 2 (normal mergers activity). The three regime model used here represents an improvement on the existing models for merger waves as it accurately replicates the different behavior exhibited by the series over time. Existing literature in the area limit itself by allowing M&As series to follow two regimes only, something that can lead to false results as far as declining mergers activity periods were included in one of the two regimes (normal or increasing activity). Whenever one of these other periods occurs, the data is more likely to flatten out, if only for a short time, before changing direction. Thus, the dominance of Regime 2 is not a surprising result, nor is the fact that this regime has the longest expected duration. More surprising, however, is the longer duration associated with Regime 1 as compared to Regime 3, suggesting that the start of a merger wave is often marked by an explosive increase in takeover activity which is considerably steeper than the drop marking the end of the wave. This offers an explanation for the failure of previous attempts to model merger waves as bubbles, and offers some interesting potential areas for future research. At a second stage the contemporaneous relationship between the Mergers and Acquisitions activity in the UK with the

Stock Market and the aggregate economic activity (Business Cycle), is found to be significant. The latter contributes to the literature as far as it is the first time the effect of the aggregate economic activity and the stock market on mergers activity is examined within a single model. However, when the relationship between the mergers and acquisitions activity, the stock market and the business cycle is examined under each one of the regimes of mergers and acquisitions activity, the evidence suggests that the relationship remains the same in all the three regimes.

At industrial level (Chapter Four) the evidence presented in the chapter suggests that most of the industrial merger and acquisition series display wave characterising autoregressive dynamics. However, in some industrial sectors a single regime identified - the one of normal merger activity. Moreover, the empirical results suggest that a relationship between the merger and acquisition activity in the UK with the Stock Market and the aggregate economic activity (Business Cycle) at sectoral level does not exist, although in chapter three a strong positive one has been identified at aggregate level. In other words, the hypothesis that the aggregate economic activity and the stock market drive the market for corporate control has not been confirmed, at industrial level. This could be a result of the small time horizon of the data set under investigation. However, M&A data at industrial level are not available for the years before 1985. The above findings contribute towards a better understanding of the Mergers and Acquisitions activity and especially, towards the view that Merger waves can be approached as a result of wave behaviour at industrial level. So far, a limited number of studies

investigated merges behaviour at industrial level and all of them assume that merges series follow two regimes only.

The above findings lead us to further investigate the issue employing alternative theories and empirical applications (chapter 4). The tests in this chapter directly compare the two explanations of merges waves (neoclassical vs behavioral) employing UK data (all previous attempts were employing USA data) and support the behavioral model. The chapter furthermore expands previous attempts by controlling for a number of documented parameters by the literature parameters. The empirical evidence suggests that stock market reactions to merger announcements in short-run are consistent with the market timing theory of merges. Taking together, the results of this chapter provide strong support to the proposition that stock market mis-valuation and the market timing ability of manager is the main driving forces behind merger activities. They also add evidence to the growing field of behavioral corporate finance that suggest that managerial decisions are primarily driven by mis-valuation of financial markets and the managers' desire to time the market. In other words the above findings posit inefficient capital markets and differences in managerial time-horizons as the key drivers of merger activity. Short-run managers sell their firm for stock in a long-run manager's firm when both firms are overvalued, even though the transaction price gives the short-run manager less than he knows his firm will be worth in the long run. The short run manager then sells his stock. The market is assumed to be irrational and therefore does not react to this deception or

exploitation. Therefore, our findings support mis-valuation theories based on behavioral explanations. Economic shocks could well be the fundamental drivers of merger activity, but mis-valuation affects how these shocks are propagated through the economy. Mis-valuation affects who buys whom.

Concluding, this thesis contributed to the understanding of mergers and acquisitions behavior to the extent that provides evidence that further supports the hypothesis that mergers in the UK come in waves. It also dates the mergers waves and provides evidence towards the assumption that corporate takeovers are driven by the aggregate economic activities and the financial market.

The above findings have several implications for economic analysis as well as for policy. It suggests that mergers and acquisitions do not always move toward greater efficiency. It shows that takeovers can be as much a manifestation of agency problems as a route to correcting them. It also demonstrates that using the stock market a gauge of profitability of corporate actions can lead one seriously astray: investors can and do make systematic mistakes. Finally, aggressive government policy - in this case antitrust policy, can have large unintended effects.

Regarding future research, the area of mergers and acquisitions is full of research potential with externalities to all areas of financial economics. More specifically, regarding the *Market Timing Theory* of mergers this thesis reports short-run evidence only for acquiring firms. However, Shleifer and Vishny (2003)

hypotheses also make clear predictions for combined CARs (target and bidder), an area that needs further investigation. Additionally, in Shleifer and Vishny's (2003) framework, though the market is mis-priced but will correct itself in the long run. If this is the case, we should not expect to observe any significant long-run performance differentials between High and Low premium sub-samples of Chapter Five. The latter is another research question that we are extremely interested to attempt to answer in the near future.

Moreover, the fast growing area of behavioral finance can be further linked with the area of mergers and acquisitions. Specifically, firms with greater expected growth uncertainty when they announce a merger decision are likely to realize lower announcement returns for at least 3 reasons: (1) Behavioral Finance. (2) Rational Expectations Models, and (3) Uncertainty Resolution. According to Miller (1977) Growth Uncertainty leads to diversity of opinion and a downward sloping demand curve for common stock, causing poor returns on equity financed acquisitions of public firms because they increase the supply of bidder's shares. Moreover, Growth uncertainty can be due to information asymmetry between corporate insiders and outside investors (Rational Expectations models). This leads to negative announcement returns for acquisitions paid for with Stock because management is likely to use stock if it's overvalued. In other words mergers, in this case, signal to the market that equity is overvalued. On the other hand acquisitions paid for with Cash overcome this problem to the extent that cash takeovers are

more favorable because the use of cash signals to the market that equity is not overvalued.

Finally, an acquisition can reduce (increase) uncertainty about a firm's growth prospects. Such uncertainty resolution can reduce (increase) firm value in some valuation models. Pastor and Veronesi (2004) suggest the firm value is increasing in growth uncertainty and falls with resolution of uncertainty in efficient markets. To the extent that highly value firms are firms with high growth uncertainty that are more sensitive to resolution of uncertainty, we expect an M&A announcement that reduces growth uncertainty to be followed by a drop in firm value unless there is a large synergy component to offset the resolution of uncertainty effect. The entire above hypothesis have never been tested in the UK or European markets. It is our intension to attempt to empirically test it in the future.

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## **Peroxide reactions of environmental relevance in aqueous solution**

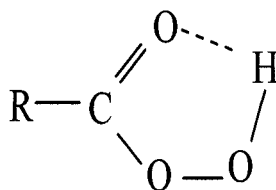
# Chapter 1

## General introduction

### 1.1 Peroxoacid

#### 1.1.1 The chemistry of peroxoacid

Organic peroxy acids are one of the most useful classes of organic peroxides due to the wide range of specific oxidation reactions that they perform, which are always high in quantitative yield. Organic peroxy acids, or peracids, are derivatives of hydrogen peroxide in which one of the hydrogen atoms is replaced by an acyl or aroyl group monoperoxy acids containing one peroxy carboxyl( $\text{CO}_3\text{H}$ ) group; diperoxy acids contain two. No examples of tri- or higher peroxy acids are known.



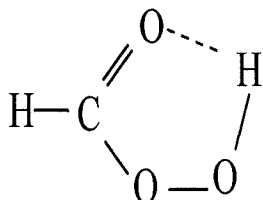
Structure [1:1]

Both dipole moment measurements of aliphatic peroxoacid<sup>[1]</sup>, and infra red spectral evidence<sup>[2]</sup>, reported that peroxoacid have, to a greater or lesser extent, a skew have been conformation about that the O - O bond in peroxides is similar to that shown in hydrogen peroxide.

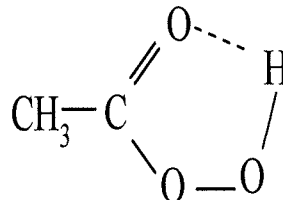
The U.V. spectra of peroxoacid are in the same way to those hydrogen peroxides, which means they exhibit a continuously increasing absorption as the wavelength decreases. In 1962 Symons has been concluded that for hydrogen peroxide the oxygen lone pair electrons or electrons in weakly "pi" ant bonding orbital's at the transitions<sup>[3]</sup>.

### 1.1.2 The systematic name

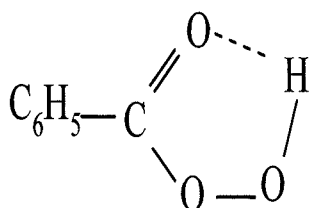
The word peracids has been in common use from long time ago and many works still use it. The systematic name, which clearly indicates the presence of peroxide oxygen in the molecule and avoids ambiguity in certain cases, is preferred.



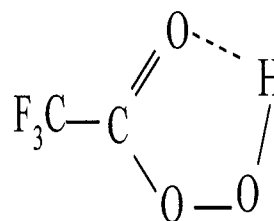
Peroxyformic acid (performic acid)



Peroxyacetic acid (peracetic acid)



Peroxybenzoic acid (perbenzoic acid)



Peroxytrifluoroacetic acid  
(Trifluoroperacetic acid)

Figure 1.1; - some typical examples of organic peroxy acids

### 1.1.3 Peroxoacid and pKa

Parent acids are generally stronger acids than the Peroxoacid. Some examples are listed below shows the pK of the acids and their respective peracids.

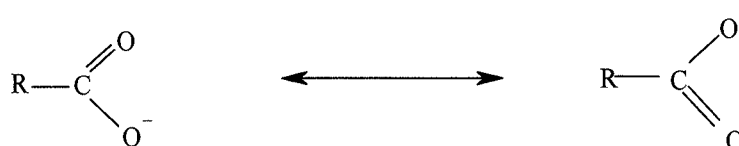
Table 1.1:- shows the peroxoacid with pKa <sup>[4]</sup>.

	pK		pKa
Formic acid	3.8	Performic acid	7.1
Acetic acid	4.7	Peracetic acid	8.2
Propionic acid	4.9	Perpropionic acid	8.1
Sulphuric acid	1.9	Peroxomonosulphuric acid	3-4

For example, peracetic acid has a pKa of 8.2 <sup>[5]</sup>, whereas acetic acid has a pKa of 4.7. There are two explanations for this.

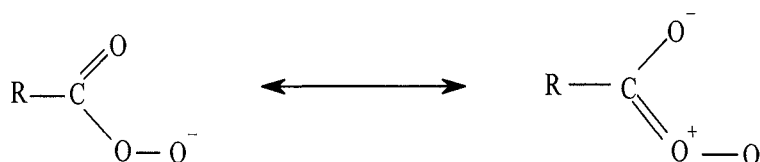
One explanation is that intermolecular hydrogen bonding stabilizes the neutral molecule relative to the anion form<sup>[6]</sup> such as structure [1:1]

The second explanation is that the parent carboxylic acid has an anion form stabilized by a delocalized electronic configuration <sup>[7]</sup>. Scheme [1:1]



*Scheme [1:1]*

Whereas canonical resonance forms would be much less likely to contribute to the peroxyanion ground state <sup>[7]</sup>.scheme [1:2]



*Scheme [1: 2]*

Moreover, the methyl substitutions in alkyl hydroperoxides and aryl substituents in Peroxybenzoic acids affect the pKa values less than in the parent of alcohols and benzoic acids respectively. This is due to that polar and electronic effects is weakened in passing through the O – O bond to affect the strength of the terminal O –H bond <sup>[5]</sup>

Since the O – O link is one atom longer and electronically saturated so this weakening of the electronic effect is not unexpected. There are other weakening is

observed in organic systems by insertion of a methylene group between substituent and reaction site.

The dissociation constants of peroxomonosulphuric acid<sup>[8]</sup> and peroxomonophosphoric acid<sup>[9]</sup> have been measured spectrophotometrically utilizing the increase in extinction in the ultra violet region on ionization of the peroxidic proton.

Due to the decomposition of the peroxyacid during the titration it is cannot be measurement of dissociation constants to a high degree of accuracy.

## 1.1.4 Peroxyacid decomposition

### 1.1.4.1 Auto decomposition

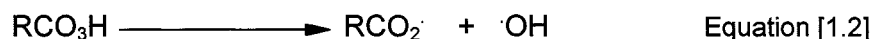
Organic peracids decompose spontaneously auto decomposition to produce parent acids and oxygen, The rate of decomposition,  $v$ , is maximised at the  $pK_a$ <sup>[10]</sup>. as can be seen in this equation.



### 1.1.4.2 Effect of thermolysis and photolysis

The thermal decomposition of peroxyacetic acid has been studied in both the vapour phase<sup>[11]</sup>, and in aromatic solvents<sup>[12]</sup>. Under these conditions the decomposition is mainly homolytic and the dissociation energy of the O-O bond has been reported from activation energies to be 30 to 34 k cal mole<sup>-1</sup>.

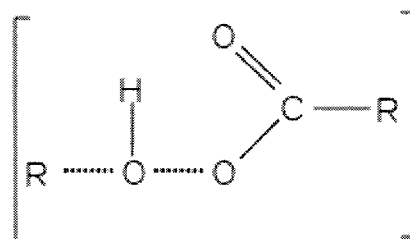
Leffort et al<sup>[13]</sup>. has been demonstrated systematically the radical decomposition of peroxyacids by thermolysis, Ando<sup>[14]</sup> have been give the most important facts for these reactions below.







Rapidly decarboxylation of the carboxy radicals in equation [1.3]. The relative reactivities of radicals with peroxyacids [1.4] correlate with their ionisation potentials, they are explained by the following polar effect in structure [1.2]

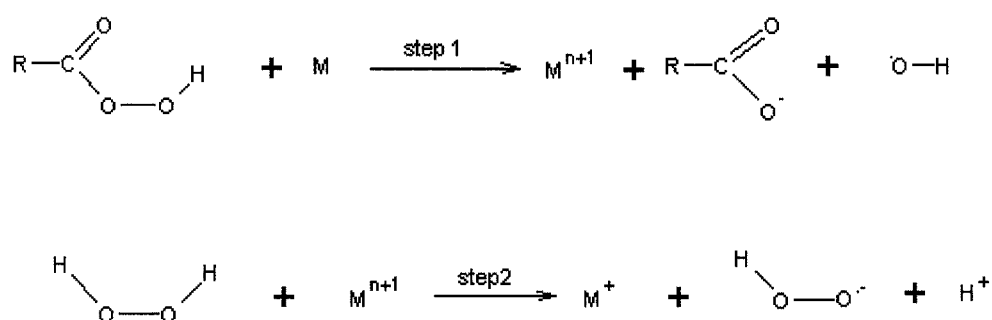


Structure [1:2]

### 1.1.4.3 Metal ion interactions

Decomposition of peroxyacid has been shown to take place in aqueous solution via free radical pathway when catalysed by metal ions of variable valence <sup>[15]</sup>.

Scheme [1: 3] below shows that hydrogen peroxide able to the catalysis of metal ion decomposition, where M is the metal ion of variable valence.



**Scheme [1: 3]:- Peroxide synergism in redox cycling with metal ions**

Ethylenediaminetetraacetic acid(EDTA), has been shown to drastically reduce the metal catalysed decomposition of peroxyacid and hydrogen peroxide <sup>[15, 16]</sup>.

Presumably by sequestering the trace metal ions, and has been used in a number of researches to reduce metal catalysed reaction.

The reaction shown in scheme [1.3] is not suppressed by Ethylene diaminetetraacetic at high pH. The discovery that polyaminopolphosphonates inhibited peroxide loss because of suspicion of radical involvement in the reaction mechanisms <sup>[17]</sup>.

### 1.1.5 The Preparation of peroxyacid

Numerous methods are known for the preparation of peroxyacids, some are general while other is specific for certain peroxyacids only these preparations are summarized in table (1.2) below.

**Table1.2:- summary of types of reaction that have been reported for preparing peroxyacids.**

	Reference
$\text{RCO}_2\text{H} + \text{H}_2\text{O}_2 \text{ (30 to 98\%)} \xrightleftharpoons{\text{H}^+} \text{RCO}_3\text{H} + \text{H}_2\text{O}$	[18-20]
$\text{RCHO} + \text{O}_2 \xrightarrow{\text{free radical chain reaction}} \text{RCO}_3\text{H}$	[21-23]
$\text{RCO}_3\text{COR} \xrightarrow{\text{Hydrolysis}} \text{RCO}_3\text{H} + \text{RCO}_2\text{H}$	[24, 25]
$\text{RCO}_2\text{COR} + \text{H}_2\text{O}_2 \longrightarrow \text{RCO}_3\text{H} + \text{RCO}_2\text{H}$	[18, 26, 27]
$\text{RCOCL} + \text{H}_2\text{O}_2 \xrightarrow{\text{base}} \text{RCO}_3\text{H} + \text{HCL}$	[18, 28, 29]
$\text{B (OCOR)}_3 + 3\text{H}_2\text{O}_2 \longrightarrow 3\text{RCO}_3\text{H} + \text{H}_3\text{BO}_3$	[18, 30]

By carefully mixing the hydrogen peroxide and carboxylic acids in the presence of an acid catalyst such as sulphuric acid, the most effective and a majority commonly used as a catalyst is the sulphuric acid or sulfonic acid type ion-exchange resins, but other acids can be used.

From table 1.2 we can see that reaction 1 is reversible, and the conversion and yields of peroxy acids are highest when the water content is at a minimum. This is accomplished either by the use more concentrated hydrogen peroxide<sup>[31]</sup>, or the use of excess aliphatic acid.

Peroxyacetic acid it is one the oldest know peroxy acids and have been prepared from long time ago 1864 by mixed diacetylene peroxide with Brodie<sup>[32]</sup>, but it was not isolated and characterized until much later in the classical work of D'Ans and his co-workers<sup>[33]</sup>.

The most important and widely used peroxy acid is the Peroxyacetic acid, therefore the number of publications and patents describing its properties, preparation and reactions.

In the early 1900s the first dilute aqueous solutions of Peroxyacetic acid were obtained by the mild hydrolysis of diacetyl peroxide<sup>[34],[35]</sup>, and of benzoylperoxide<sup>[36]</sup> due to the reaction of diacetyl peroxide with dilute aqueous hydrogen peroxide<sup>[37]</sup> or by the reaction of diacetyl peroxide with base followed by acidification. In 1945 the reaction of acetic anhydride with an inorganic peroxide or with dilute solution of hydrogen peroxide has been used to obtain dilute solutions of Peroxyacetic acid or its salts<sup>[38]</sup>.

#### **1.1.5.1 Direct Preparation from acetic acid**

Reaction 1, table 1.2 shows that the direct acid catalyzed reaction of 30 to 98% hydrogen peroxide with acetic acid to preparation of peroxy acetic, this method was the most important and widely used to preparation of Peroxyacetic acid, the acid catalyzed formation and hydrolysis of peroxy acetic acid is bimolecular and involves acyl-oxygen cleavage<sup>[39]</sup>. the specific reaction rate constant at the formation of Peroxyacetic acid from acetic acid and hydrogen peroxide is reported to be  $7.4 \times 10^{-6}$

liters mole<sup>-1</sup> sec<sup>-1</sup> this is at temperature 25<sup>0</sup>C [40], in the presence of 2% by weight of sulphuric acid.

Pungor and co-workers<sup>[41]</sup> have been published the rate constants at higher reaction temperatures and at varying hydrogen peroxide concentration and water. Sulphuric acid as well as has been used as a solvent reaction medium for preparing peroxy acetic acid [42-44]. But the disadvantage have been seen from using large quantities of sulphuric acid with carboxylic leads to miscible with hydrogen peroxide, for this reason the use of more sulphuric acid or other catalysts such as nitric ,hydrofluoric, and phosphoric acids than is need to speed up peroxy acid formation is unnecessary complication.

The equilibrium constant for the preparation of Peroxyacetic acid from acetic acid and hydrogen peroxide is somewhat uncertain. Values ranging from approximately 3<sup>[45]</sup> to 7<sup>[33]</sup> have been reported in the temperature range 0 to 25<sup>0</sup>C. The main three effects that related to the equilibrium constant for Peroxyacetic acid formation is sulphuric acid hydrogen peroxide concentration and temperature<sup>[46],[47]</sup>.As anhydrous conditions are approached, the equilibrium constant is reported to increase to approximately 4.5 at 25<sup>0</sup>C [47].The variation in values has been attributed to analytical difficulties and decomposition with loss of active oxygen. In 1965 Sawaki and Ogata<sup>[48]</sup> has been confirmed that the increase in the concentration of sulphuric acid leads to increase in equilibrium constant (K).

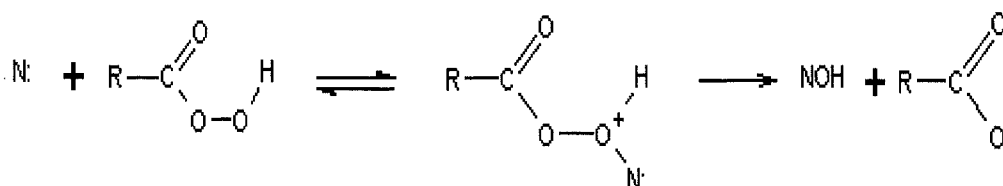
### **1.1.6 The electrophilic of peroxyacid**

Peroxyacid are ambident electrophiles and attack either takes places at the outer peroxides oxygen or at carbonyl carbon.

#### **1.1.6.1The outer peroxidic oxygen**

The outer peroxidic oxygen has non bonded electrons and reacts faster with polarisable Soft nucleophiles it is reacts much faster with Iodide than chloride<sup>[49]</sup> The electrophilic oxidation of azobenzene by peroxobenzoic acid in benzene produces azoxybenzene. The second order rate constant is  $2.31 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ . the rate increases with electron donating substituents on the azobenzene<sup>[50]</sup>.

As there is many reducing agents are nucleophiles, oxidation may take place by displacement mechanism on the oxygen ,in 1962 Edwards<sup>[51]</sup> proposed A simple model for the transition state see Scheme [1: 4] below.



**Scheme [1: 4]:- A simple model for transition state**

From this model there are many predications are possible such as;-

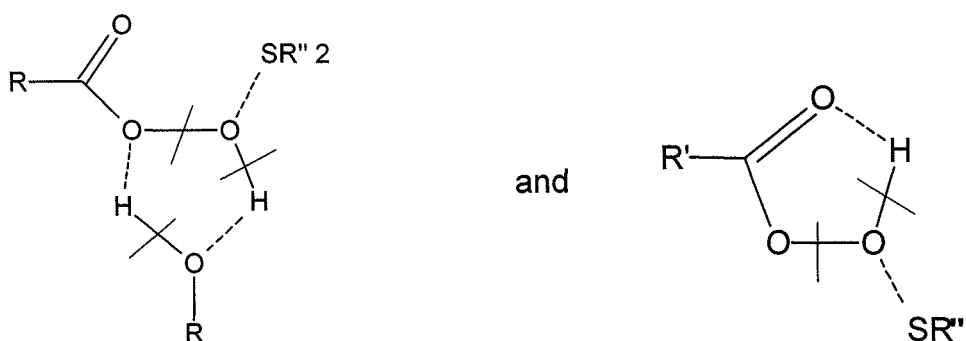
- The entropy of activation should be negative.
- Less basic leaving groups  $\text{RCOO}^-$  should increase.
- Since there is unshared electron pair on the oxygen atoms various types of acid catalysis should be apparent.

The above properties have shown in acidic solutions when oxidations of halides such as the oxidations of chloride and bromide ions by peroxyacetic, peroxomonosulphuric acids<sup>[49]</sup> or iodide by substituted peroxobenzoic acids<sup>[52]</sup>.

The slopes of the plots of log second order rate constant against the pKa of the parent acid are -0.5 the electron withdrawing groups increase the rate. The magnitude of the effect is less than is generally the case but consistent with results produced for other hydroperoxides and halide ions<sup>[51]</sup>.

In reactions such as the oxidation of Olefins to epoxides and sulphides to Sulphoxides the scheme suggested by Edwards above is even less satisfactory energetically than in the case of halides or other negatively charged nucleophiles since it involves charge separation in going from reactants to products.

In 1970 Edwards<sup>[53]</sup> proposed that these reactions are influenced by solvation of the ground state both of the substrate and peroxyacid also the transition state. And proposed structures, Scheme [1: 5], for the transition state in both protic and aprotic solvents which involve by passing of charge separation.

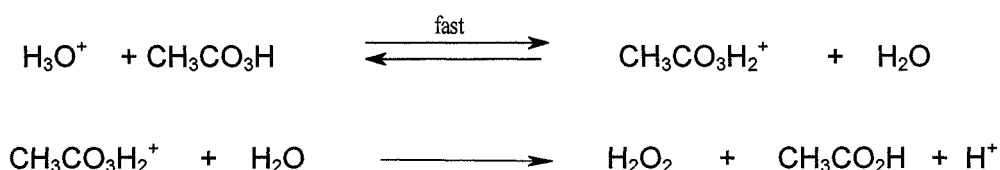


**Scheme [1: 5]:- the transition state in both protic and aprotic solvents.**

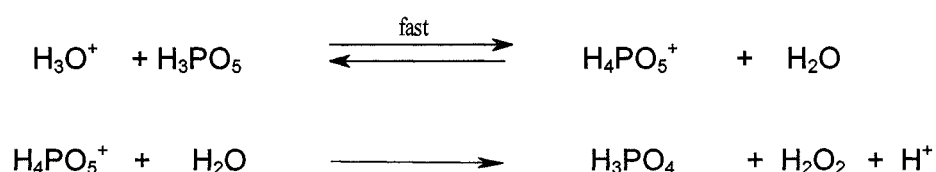
There are many studies shows the transition states is similar to those suggested by Edwards such as oxidation of sulphines to ketones<sup>[54]</sup> and acetylenes<sup>[55]</sup>.

### 1.1.6.2 The carbonyl carbon in peroxy acids

The carbonyl carbon is relatively *hard* since it has some positively charged character. It reacts with hard charged non – polarisable bases such as hydroxide. The transition state consisted of nucleophilic attack of water on the conjugate acid of the peroxyacetic acid in 1956 Bunton<sup>[56]</sup> studied the hydrolysis of peroxyacetic acid and found it to be acid catalysed.



The similar conclusion for the hydrolysis of peroxomonophosphoric acid have been reported by Battaglia and Edwards<sup>[9]</sup> and they suggested the possibility of a non acid catalysed pathway but under the conditions necessary to measure this the decomposition of the peroxyacid was the predominant reaction.



By using an  $^{18}\text{O}$  isotope label<sup>[56]</sup> and the mechanisms proposed for the peracetic acid synthesis and hydrolysis it has been shown that<sup>[48, 57, 58]</sup> the reaction did not involve dissociation of the O-O bond in the initial hydrogen peroxide, Bunton et al in 1956 was proved conclusively using  $\text{H}_2^{18}\text{O}$  as solvent that hydrolysis involves cleavage of the carbon-oxygen bond, this means that the acyl group and oxygen atom is cleaved in both of the formation and hydrolysis of peroxyacids



### 1.1.7 Oxidation Capacity of Selected Sanitizers

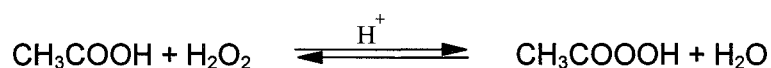
The peracetic acid is stronger oxidizer and have a higher oxidation potential more than chlorine dioxide and sodium hypochlorite but less than ozone, therefore the peracids inactivates which that responsible for degradation, the table(1.3) below shows that the oxidation capacity of peracids.

**Table1.3 :- shows the oxidation Capacity of Selected Sanitizers.**

Sanitizer	eV*
Ozone	2.07
Peracetic Acid	1.81
Chlorine dioxide	1.57
Sodium hypochlorite (chlorine bleach)	1.36

### 1.1.8 Peroxide determination Techniques

Peracetic acid is a strong oxidizer most analytical techniques for peracetic acid are based on the redox properties of the acid. This is due to the acid-catalysed equilibrium shows equation below,

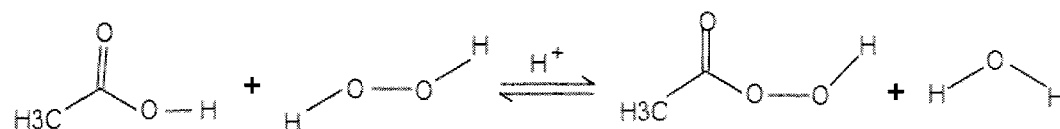


Hydrogen peroxide is always present in peracetic acid solution this is because of the peracetic acid is technically synthesized by mixing concentration solution of acetic acid and hydrogen peroxide in the presence of sulphuric acid as catalyst. The quantitative determination of peracids is difficult, because watery peracids solutions always contain hydrogen peroxide, which shows similar reactions. So hydrogen peroxide and peracids are high reactive oxidising agents and have similar reactivities with many reagents used in peroxide determination making resolution of a mixture of these peroxides difficult. for example the uncatalyzed reaction of peracetic acid and  $I^-$  is by 5 orders of magnitude large than of hydrogen peroxide with  $I^-$  <sup>[59]</sup>. Therefore, the development of a fast and reliable method for the determination of PAA in aqueous solutions is of great interest.

Various methods have been reported for the determination of peracetic acid in acidic solution, the most widely used methods for analyzing solution containing peracetic acid and hydrogen peroxide are ,Titration methods by D'Ans and Frey<sup>[60]</sup> and its modification by Greenspan and Mckellar<sup>[61]</sup> , and this method utilized by sully and Williams<sup>[62]</sup>.

Conductivity measurements, photometry <sup>[63-66]</sup>. Spectrophotometry <sup>[67-69]</sup> . gas and liquid chromatography determination <sup>[70-73]</sup>. Electrochemical sensors measurements<sup>[74-77]</sup>.

D'Ans and Frey<sup>[60]</sup> have been described methods for the analysing solution containing peracetic acid and hydrogen peroxide .in this method the hydrogen peroxide is first titrated with permanganate and then adding potassium iodide to determined the peracetic acid with titration the liberated iodine with thiosulphate.

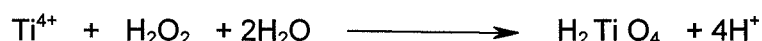


**Scheme [1: 6]:- Acid- catalysed equilibrium**



In 1948 Greenspan and Mackellar <sup>[61]</sup> have been utilized a similar method to determine peracetic acid in the presence of hydrogen peroxide, which first titrating the hydrogen peroxide with ceric sulphate(IV) (ammonium tetra sulfatocerate), followed by an iodometric determination of the residual peracetic acid present and this method utilized by sully and Williams <sup>[62]</sup> to avoid significant equilibration of the peroxide in the acidic conditions the titrations must be carried out rapidly with temperature below 10° C <sup>[62]</sup> and much greater reactivity of iodide with peracetic acid than with hydrogen peroxide Therefore, liberated iodine by titrated with 0.1N sodium thiosulphate this was repeated several times about 10 minutes by plotting titration versus time and extrapolating back to zero time to obtained the corrected titre corresponding to the peracetic acid present and calculate hydrogen peroxide from total titration this method is widely used to resolve solution containing peracetic acid and hydrogen peroxide consequently, the reliability of this method is gives very good results when concentrations of the two peroxo species are comparable,

In 1943 Eisenberg have described<sup>[78]</sup> a Colorimetric method for the determination of low levels of hydrogen peroxide concentration as low as  $5.29 \times 10^{-5}$  M involves reaction with acidified, which utilizes the yellow coloured complex produced between the titanium (IV) ion and hydrogen peroxide with maximum absorption at 400nm according to the reaction below



The complex of Titanium is often written as  $\text{TiO}_2^{2+}$  <sup>[79]</sup> the titanium (IV) complex methodis selective for hydrogen peroxide at room temperature, at high temperature the colour development is proportional to the total peroxide concentration in a solution<sup>[80]</sup>. Ogleby and Williams<sup>[80]</sup>has been applied to use this property to measure concentration of amixed solution from peracetic acid and hydrogen peroxide (approximately 15% PAA, 14%  $\text{H}_2\text{O}_2$ ) the solution will be divided into samples one heated to (90-95 c) and second one cold which remains at room temperature, then the titanium (IV) oxide assay reagent is added simultaneously and the colour development in the two samples compared, allowing the calculation of the respective percentages of the two peroxides which means the colour development, The colour development in the two pairs, the colour developed in the pair without

heating is proportional to the hydrogen peroxide content of the sample but the colour developed in the pair heated is proportional to the total peroxide content in the sample the resulting difference signal from the colorimeter is proportional to the peracetic acid content of the sample this method measuring peracetic acid in the range 1-500mg L<sup>-1</sup> .in practice , in a fully automated system, sodium molybdate, which reacts with peroxides in a similar way, replaced the titanium (IV) oxalate which is unstable especially at high temperatures.

In 1959 Saltzman and Gilbert<sup>[68]</sup> have been developed the basic technique of kinetic Colorimetry for the determination of microgram quantities of peroxides by distinguished between hydrogen peroxide and peracetic acid using neutral potassium iodide reagent,

This technique applicable to resolve mixtures of peroxides obtained from atmospheric samples<sup>[68, 81, 82]</sup>.

In 1983 Frew et al<sup>[65]</sup> have been studied the development of quantitative Spectrophotometric method for the determination of peroxides in the concentration range as low as 1 - 10μM (10<sup>-6</sup> – 10<sup>-5</sup> mol dm<sup>-3</sup>) this method based on four assays, (1) based on formation of phenolphthalein or triiodide, (2) iodide oxidation catalytic dye bleaching, (3) coupled oxidation of NADPH, (4) Horseradish peroxidase-coupled oxidations. The four methods in which the reactions with hydrogen peroxide and peracetic acid has been compared the only for the coupled oxidation of NADPH assay significant colour development was found when using metachloroperbenzoic acid (MCPBA) but the other three showed no selectivity for hydrogen peroxide at all.

Davies and Deary<sup>[67]</sup> in 1988 have been determination of peracetic acid in the presence of up to a 1000-fold excess of hydrogen peroxide by using Spectrophotometric method.

This method is similar to the titrimetric method of Sully and Williams, therefore, involves extrapolation of the absorbance change caused by the initial rate of the reaction between hydrogen peroxide and iodide, back to zero time to give a value that similar to the iodine formed due to reaction of the peracid and iodide, this method has been used in the study of the formation of peracetic acid during the perhydrolysis of PNPA.

Flow injection analysis is another method to achieve a continuous observation of the peracetic acid level.

Krussmann and Bohnen<sup>[63]</sup> has been used the peracetic acid to oxidation of iodide to the coloured triiodide ion to detect the peracid. As hydrogen peroxide would lead to false positive results, it is decomposed by the catalase before to the reaction with iodide, therefore requiring an additional reaction step.

Harms and Karst<sup>[83]</sup>, have been development of a very simple flow injection analysis(FIA) methods to determination of peracetic acid this method based on a selective reaction between the peracid and the reagent. The selective oxidation of used for this method is 2, 20-Azino-bis (3-ethylbenzothiazoline)-6- sulphate) (ABTS) with peracetic acid under formation of a green coloured radical cation (ABTS<sup>•+</sup>). Major advantages of this method are the simple experimental setup and the high selectivity towards hydrogen peroxide in the presence of iodide as catalyst at room temperature.

In 1984 Di Furia et al<sup>[84]</sup> found that the Ce(IV) methods fails to give accurate results to determined very small amounts of peracetic acid in solution in the presence of large excess of hydrogen peroxide ,and he was developed anew method which is used a gas – liquid chromatographic method for the determination of peracetic acid in the presence of large excess of hydrogen peroxide and the procedure for this method based on the fact that, the oxidation of an organic sulphide to the corresponding Sulfoxides is very slowly with hydrogen peroxide but very fast with peracetic acid. on this basis, a known excess of sulphide is added to the solution from peracid and hydrogen peroxide the reduction of the peracid within a few seconds whereas hydrogen peroxide is not consumed then by gas- liquid chromatographic measurement the concentration of the peracid from the remaining sulphide concentration and the amount of Sulfoxides formed, simultaneously measured by gas – liquid chromatographic. This method has been applied to determination of 0.002M peracid concentrations (m-chloroperbenzoic acid) in the presence of up to one hundred – fold excess of hydrogen peroxide.

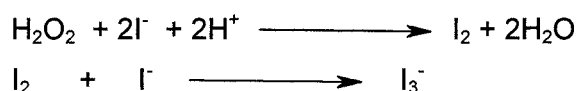
Pinkernell et al has been developed a chromatographic method to determination of peracetic acid and hydrogen peroxide (simultaneous determination) and this method based on the selective oxidation by two reactions step. The first step by using peracetic acid to oxidation of Methyl-p-tolylsulfide (MTS) to the corresponding sulfoxide (MTSO).

In second step by using hydrogen peroxide to oxidize triphenyl phosphine (TPP) to the corresponding phosphine (TPPO) then can be easily separated all these four compounds by liquid chromatography (LC) with UV detection. The reagents are used as the base for the development of a direct simultaneous method for the LC determination of peracetic acid and hydrogen peroxide in alkaline media. This method required to derivatization of peracetic acid by MTS a pH range between 2 and 6 is required but for hydrogen peroxide the pH required range between 2 and 10.5. So the alkaline samples have to be buffered prior to analysis for using this method therefore there are many disadvantages such as equilibria involving peracetic acid and hydrogen peroxide maybe influenced<sup>[85]</sup> and changes in sample composition may occur based on pH change.

Effkemann in 1998<sup>[86]</sup> by using liquid chromatographic was developed the MPSO/TPP method as the ideal method for the simultaneous determination of hydrogen peroxide and peracetic acid in alkaline media without pH change prior to analysis.

Direct determination of peracetic acid, hydrogen peroxide and acetic acid in disinfectant solutions of peracetic acid and is very simple and rapid in the spectral measurements and analysis by Far-ultraviolet absorption spectroscopy<sup>[87]</sup>, the principle of this method is not required any reagents or catalysts, a calibration standard or any other complicated procedure for analysis. The only required preparation a dilution of hydrogen peroxide with pure water at concentration range lower than 0.2 wt % in sample solutions this method could achieve the detection limit (0.002, 0.003 and 0.01 wt%) peracetic acid , hydrogen peroxide and acetic acid respectively and the response time for the simultaneous determination of the three species in 30s

Also there are another technique recently used to determination of hydrogen peroxide and peracetic acid by using coupled charge device (CCD) Technologies<sup>[88]</sup> This method based on the separation of peracetic acid and hydrogen peroxide on a reverse phase HPLC system followed by post-column reaction with a concentrated solution of potassium iodide as the reaction below with ammonium molybdate as catalyst.



The higher molar absorptivity of  $\text{I}_3^-$  ( $26500 \text{ M}^{-1}.\text{cm}^{-1}$ ) and the detection limit at 352nm HPLC conditions was  $10^{-6} \text{ M}$  levels.

Determination of peracetic acid by flow injection analysis<sup>[89]</sup> [FIA] this method based on a selective reaction between the peracid and the reagent, and suitable for analysis of large numbers of samples in short period of time and for on-line determination of peracetic acid samples especially in industrial processes.

Not all previous techniques have high selectivity and low detection limits, such as Titration methods it is not applied to use when measuring very small amounts of peracetic acid in solution contains a large excess of hydrogen peroxide if used can give some errors, but applied to use at relatively high concentrations.

Photometric, Spectrophotometric and conductivity measurements methods are required a calibration by using peracetic acid as standard solution we know when diluted aqueous solutions of peracetic acid are unstable, another problem is the considerable reactivity toward hydrogen peroxide, also these methods lack for selectivity.

Chromatographic methods have a low detection limit, negligible reactivity toward hydrogen peroxide and can be analyze peracetic acid in the presence of a large excess of hydrogen peroxide in both acidic and alkaline<sup>[71]</sup> media, the problem is time-consuming because of the need for an extraction step with chloroform a solution suitable for gas chromatography.

The main method of peracetic acid measurement employed throughout the course of this research has been based on the titration method in chapter two the formation of peracetic acid and total peroxide content is determined by iodimetric titration, where the peracetic acid reacts with iodine ion faster than hydrogen peroxide. The reaction is carried out in the presence of starch. The initial release of  $I_2$  is measured by this titration then ammonium molybdate catalyst is added and the  $I_2$  released is further titrated with thiosulphate.

## 1.2 Dyes

Decomposition and hydrolysis of peracetic acid are undesirable since they lead to the formation of products which have no bleaching action; the bleaching action of peracetic acid is mainly the result of epoxidation of the double bonds present in unwanted coloured compounds<sup>[64, 90]</sup>. In chapter three we consider the oxidation of a range of azo, disazo, triarylmethane, quinoline xanthene, indigoid and anthraquinone dyes by hydrogen peroxide or peracetic acid in the presence of different transition metals, and examine the structural features that hinder or contribute to their destruction. The metals used are: Fe(III), Cu(II), Mn(III) and Ag(I). The selection of metal was based on the fact that the transition metals, particularly those possessing two or more valence states between which there is a suitable oxidation-reduction potential, can react with peracetic acid. The metals are also easily obtainable, inexpensive, and relatively low in toxicity. The use of peracids as oxidative systems for dyes, with or without metals, has thus far attracted little interest despite the use of peracid as low temperature oxidants in detergency and other applications for the last two decades. Therefore in this chapter I will be introduction of dyes

Dyes are a kind of organic compound with complex aromatic molecular structures, and like all chemicals, they are similar in their reactions to some other chemicals, and distinctly different from others.

Dyes pollutants disposed to surface water from industrial wastewater. Dye manufacturing plants, textile plants, printing and paper mills discharge their effluent containing dyes into the aqueous environment. Many of these dyes are toxic and

carcinogenic to human. The textile industry plays a major role in the economy in many countries. A very small amount of dye in the water is highly visible and can be toxic to the life in the water, in the textile industry, large quantities of aqueous wastes and dye effluents are discharged from the dyeing process with strong persistent color and high biological oxygen demand (BOD). Due to complex nature of the dyes, wastewaters become bio-resistant. About 1–20% of the total world production of dyes is lost during the dyeing process<sup>[91]</sup>, and is released in the textile effluents. The release of those colored waste waters in the environment is a considerable can originate dangerous by products through oxidation, hydrolysis, or other techniques taking place in the wastewater phase.

### 1.2.1 Colour in dyes

Dyes are characterised in accordance with their capacity to absorb the energy of a particular part of the electromagnetic radiation to which the human eye is sensitive<sup>[92]</sup>. Thus, the colour of the dye is caused by absorbance of electromagnetic radiation. Dyes are aromatic compounds, and the structure fundamentally based on the structure of benzene, as we know, benzene appears to be colourless fluid, In fact it absorbs electromagnetic radiation just as dyes do, but it does so at about 200nm so that we do not see it, at wavelengths between about  $\approx 350 - 750\text{nm}$  when an object absorbs some of the radiation from within that range we see the waves that are left over, and the object appears coloured, the wavelengths just outside the visible range are considered colourless, the colour in dyes to presence of a Chromophore which

delocalised electron systems with conjugated double bond, these are responsible for the absorption of electromagnetic radiation of varying wavelengths, chromophores do not make dyes coloured in the sense that confer on them the ability to absorb radiation rather, chromophores function by altering the energy in the delocalised electron cloud of the dye chromophores,  $-\text{C}=\text{C}-$ ,  $-\text{C}=\text{O}$ ,  $-\text{C}=\text{O}$ ,  $-\text{C}=\text{S}$ ,  $-\text{N}=\text{N}-$ ,  $-\text{N}=\text{O}$ ,  $-\text{NO}_2$ ,  $-\text{C}=\text{NH}$ .

Auxochromes are groups which attach to non ionising compounds yet retain their ability to ionise. The word auxochrome comes from auxo which means increased and chrome means colour, so the word is colour increaser , thus, auxochromes, electron- withdrawing or electron donating substituents that cause or intensify the

colour of the chromophore by altering the overall energy of the electron system as summarize the groups which are essential for production of colour is called chromophores and another groups improved the colour called auxochromes , auxochroms such as  $-OH$ ,  $-NR_2$ ,  $-NHR$ ,  $-NH_3$ ,  $-COOH$  and  $-SO_3H$  groups<sup>[93]</sup>. The table (1.4) shows the colour absorbance spectrums.

There are many ways in which colourants cause problems in water

- Concentration of dyes and depending on exposure time.
- Visibility of dyes in water depending on their colour, extinction coefficient and on the clarity of the water
- Dyes absorption and reflection of sunlight entering the water led to the greatest environment concern.

**Table1.4 :- colour absorbance spectrum (Adapted from <sup>[94]</sup>, p254).**

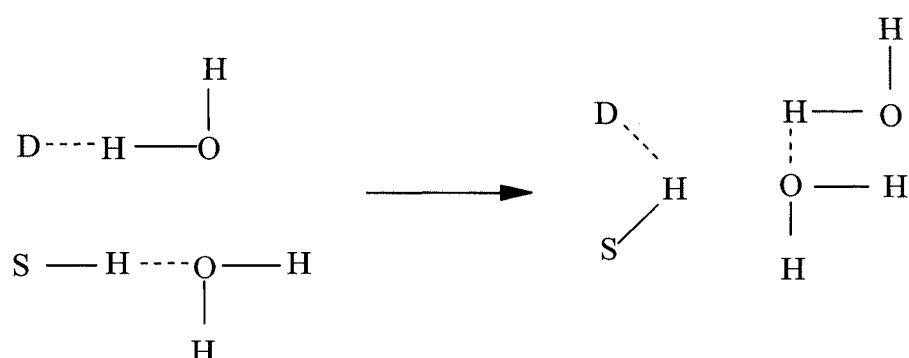
<b>Wavelength of Light absorbed nm</b>	<b>Absorbed light</b>	<b>Visible colour</b>
400 – 435	Violet	<i>Yellowish Green</i>
435 – 480	Blue	<i>Yellow</i>
480 – 490	Greenish Blue	<i>Orange</i>
490 – 500	Bluish Green	<i>Red</i>
500 – 560	Green	<i>Purple</i>
560 – 580	Yellowish Green	<i>Violet</i>
580 – 595	Yellow	<i>Blue</i>
595 – 605	Orange	<i>Greenish Blue</i>
605 - 750	<i>Red</i>	<i>Bluish Green</i>



## 1.2.2 Hydrogen bonds and dyes

Hydrogen bonding occurs when an atom of hydrogen is attracted by rather strong forces to two atoms instead of only one. Typically hydrogen bonding occurs where the partially positively charged hydrogen atom lies between partially negatively charged oxygen and nitrogen atoms, also between fluorine atom in  $\text{HF}_2^-$  and between water and halide ions for example,  $\text{HO-H}\dots\text{Br}^-$ . This is much quoted in discussions of dye

Binding by substrates when a covalently bound hydrogen atom exists between two electronegative atoms, a hydrogen bond maybe formed. Since appropriate group, e.g.  $\bullet\text{OH}$ ,  $\text{NHR}$ ,  $\text{CF}_3$  etc., are fairly common in dye molecules and substrates it is not surprising that hydrogen bonding should be postulated as a potential binding force for dyes in aggregates and with substrates. The strength of a hydrogen bond depends upon the electronegativity of the bond atoms, therefore  $\text{RNH}_3^+$  contains a more powerful hydrogen bonding atom than  $\text{RNH}_2$ . Hydrogen bond formed between dye molecule and substrate in aqueous medium then the hydrogen bonding require breaking the water hydrogen bonds also hydrogen bonding group in the substrate with the dye molecule will again require hydrogen bonds to be broken, this is aqueous system, hydrogen bonding between dye and substrate will require two hydrogen bonds to be broken for each one formed then will be after two broken hydrogen bonds two water molecules freed to bond together see Scheme [1: 7] below<sup>[95]</sup>.



**Scheme [1: 7]**

### 1.2.3 The molecular excitation model of dye and Aggregation of dye in solution

The change in the absorption spectra of many dyes with changes in concentration, temperature and ionic strength of their aqueous solutions has long been attributed to the tendency of dyes to form dimers or higher aggregates in solution there are a large difference between the absorption spectra of dye aggregates when compared with individual molecules<sup>[96]</sup> this is due to exciton coupling between the transition dipole moment of the individual characteristics molecules<sup>[97]</sup>.

The molecular exciton model qualitatively explains the spectral properties of dye aggregates the individual characteristics in the aggregates of dyes should be preserved by chromophores the transition moment of the electronic transition is assumed to be

Localized in the center of the chromophore and its polarization axis parallel to the long axis of the chromophore.

There are many forces between ions and molecules in aqueous solutions Electrostatic interactions between a oppositely charged species and repulsion between the same ions, interaction between "pi" electron systems of adjacent molecules hydrogen bonding also repulsive forces at short distances

### 1.2.4 Classifications of dye

There are two classification of dye<sup>[92, 94]</sup>

- chemical structure (chemical classification) is used by the practising dye chemists who use terms such as azo-dye , anthraquinone dyes or phthalocyanine dyes
- classification by usage or application (colouristic classification) are used by technologists such as reactive dyes for cotton and disperse dyes for polyester, dyes classified according to this method may be anionic, direct or disperse depending on their terminal application.

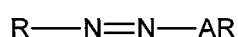
### 1.2.4.1 Colour index classification

The society of dye and colourists and the American association of textile chemists and colorists have been classified the dyes since 1924 and revised every three months this classification according to the terms of dye colour, structure and application method, Thus all dye are assigned in colour index classification number and each different dye is given a C.I generic name determined by colour and application characteristics also many of dyes and pigments in colour index are placed in one of the 25 structural classes according to their chemical type<sup>[98]</sup>.

Azo dyes (monoazo, disazo, triazo, polyazo) Monoazo dyes have only one N=N double bond, while diazo and triazo dyes contain two and three N=N double bonds, Azo dyes are subdivided into four sections due to the largest class azo dye contain one and three azo linkages , phenyl, naphthyl rings this linkages substituted with functional groups including chloro, hydroxyl, methyl nitro and sulphonate<sup>[99]</sup>. Anthraquinon dye these dyes constitute the second largest dyes in colour index.

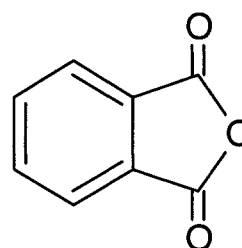
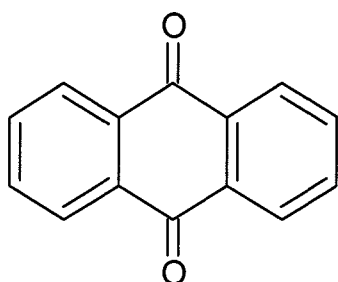
Also phthalocyanine and triarylmethane dyes are quantitatively the most important groups, other groups such as diarylmethane, indigoid, azine, oxazine, thiazine , xanthenes, nitro, nitroso, aminoketone and hydroxy ketone dyes, *Figures (1.2)* shows the most important groups of dyes.

All of these structures allow “ $\pi$ ”. “ $\pi$ ”<sup>\*</sup> transitions in UV- visible(UV-Vis) area, with high extinction coefficients that allow us to consider these structures.

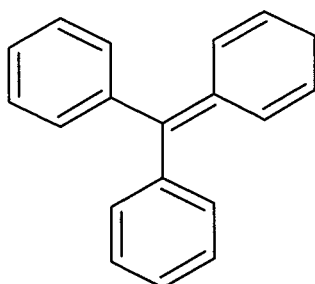


The general structure of the azo dye molecule

(Where R can be an aryl, heteroaryl or  $-CH=C(OH)$  - alkyl derivative)

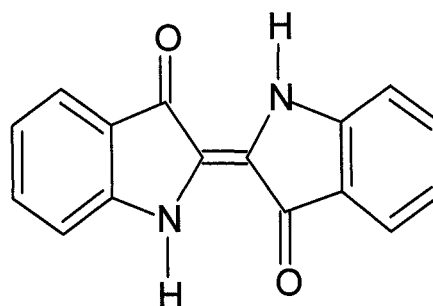


The general structures of Anthraquinone



The general structures of Triarylmethane

the general structures of Phthalocyanine



the general structures of Indigo

Figure1.2 show the general structure formulas of several different dyes.

#### 1.2.4.1.1 Acid dyes

Most acid dyes are azo (yellow to red) and the largest class of dyes in the colour Index. Acid dyes are anionic compounds. That is applied to fibers such as silk, wool. The word "acid" refers to the pH in acid dye dyebaths rather than to the presence of acid group carboxyl, sulphonate or amino in the molecular structure making them soluble in water. The chemistry of acid dyes is quite complex dyes are normally very large aromatic molecules consisting of many linked rings. Acid dyes having structures related to triphenylmethane predominate in the milling class of dyes, and many acid dyes are synthesised from chemical intermediates which form anthraquinone like structures as their final state.

#### 1.2.4.1.2 Reactive dyes

In the colour Index classification, the reactive dyes form the second largest dye class with respect to the amount of active entries, the reactive group in dye reactive is often a heterocyclic aromatic ring substituted with chloride or fluoride and this reactive groups in dyes that form double bonds with  $-OH$ ,  $-NH$ , or  $-SH$  groups in fibres. Reactive dyes first appeared commercially in 1956, after their invention in 1954 by Ratte and Stephens. In reactive dye a chromophore contains a substituent that is activated and allowed to directly react to the surface of the substrate. Reactive dyeing is now the most important method for the coloration of cellulosic

fibres, and are the most common dyes used in the textile industry due to their bright colours, good colourfastness and ease of application<sup>[100, 101]</sup>. Reactive dyes are the principal dyes used in the cotton industry which makes up 50% of the world's fiber consumption<sup>[102]</sup>. Most of reactive dyes are azo dyes. Shore in 1990<sup>[103]</sup> Reported that the reactive dye structures are 95 percent azo dyes, or metal complex azo compounds that are linked by an azo group<sup>[104]</sup>. But also anthraquinone and phthalocyanine reactive dyes applied a number of reactive dyes are toxic to many organisms and can cause direct destruction of aquatic life due to the presence of aromatic and metal chlorides<sup>[105]</sup>.

#### **1.2.4.1.3 Direct dyes**

In color Index, the direct dyes form the second largest dye class with refer to the amount of different dyes: approximately 1600 direct dyes are listed. Many of direct dyes are azo dyes with more than one azo bond or phthalocyanine, oxazine compounds; direct dyes are used on cotton, paper. They are also used as pH indicators and as biological stains. Direct dyes are usually negatively charged, in other words the coloured part of the molecule is the anion. Direct dyes are normally carried out in a neutral or slightly alkaline dye bath at or near boiling point with addition of either sodium chloride or sodium sulphate.

#### **1.2.4.1.4 Basic dyes**

In colour index, basic dyes represent about 5% of all dyes listed in the colour index. Basic dyes are water-soluble cationic dye compounds that are used for dyeing acid-group containing fibres. Basic dyes are also used in the coloration of paper. Example for basic dye, diarylmethane, triarylmethanes, anthraquinone or azo compounds. Basic dyes have amino groups, or alkylamino groups, as their auxochromes and consequently have an overall positive charge.

#### **1.2.4.1.5 Disperse dye**

In colour Index classification, disperse dyes form the third largest group of dyes, approximately 1400 different compounds are listed, disperse dyes are usually small azo or nitro compounds, anthraquinones or metal complex azo compounds,

disperse dyes were originally developed for the dyeing of cellulose acetate, and are substantially water insoluble.

#### **1.2.4.1.6 Metal complex dyes**

In colour index, metal complex dyes are usually azo compounds as aspirate category. Metal complex dyes are strong complexes of one metal atom like copper, cobalt, nickel or chromium and one or two dye molecules.

#### **1.2.4.1.7 Mordant dyes**

The use of mordant dyes is slowly decreasing about 23% of the ~600 different mordant dyes listed in the colour index are in current production. Many mordant dyes are azo, oxazine or triarylmethane compounds, the mordant; potassium dichromate is applied as an after treatment. It is important to refer that many mordant's, especially those in the heavy metal category, can be hazardous to health and more care must be taken when used.

#### **1.2.4.1.8 Pigment dyes**

Approximately 25% of commercial dye names listed in the colour index are pigment dyes, pigment dyes are insoluble, non-ionic compounds or insoluble salts this is due to their crystalline or particulate structure because of their application. The majority of pigment dyes are azo compounds or metal complex and anthraquinone.

#### **1.2.4.1.9 Vat dyes**

Most of vat dyes are anthraquinones or indigoids vat respect to the vats that were used for the reduction of indigo plants through fermentation. Vat dyes are water insoluble dyes. Most vat dyes are less suitable than fiber reactive dyes; indigo is an example of this dye class, vat dyes are widely used for dyeing cellulose fibres.

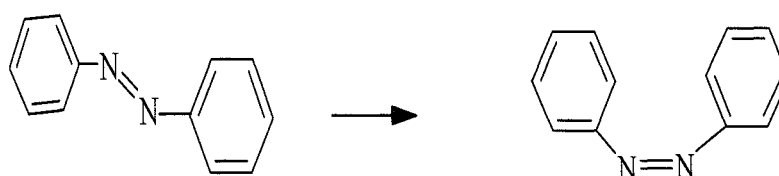
#### 1.2.4.1.10 Solvent dyes

Most of solvent dyes are diazo compounds and non-ionic dyes that are used for dyeing substrates. They are frequently called *lysochrome* dyes. The prefix *lyso* means dissolve, and *chrome* means colour. Solvent dyes are soluble in organic solvents but insoluble in water.

### 1.2.5 Isomerism in azo dye

#### 1.2.5.1 Geometrical isomerisms

Isomerisms are dyes compounds with the same molecular formula but different structural formula



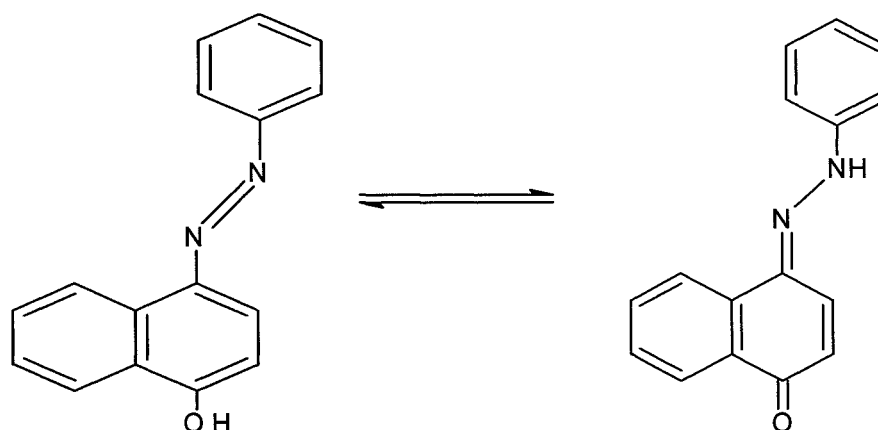
Scheme [1: 8]

#### 1.2.5.2 Tautomerism

Tautomerism are structural isomers of the same chemical substance that spontaneously interconvert with each other and have different chemical properties.

The product obtained from the condensation reaction of phenyl hydrazine with 1, 4-naphthoquinone is the same product obtained from the coupling reaction of benzene diazonium chloride with naphthol<sup>[106]</sup>, the two products gave the azo form in coupling reaction and hydrazone form in condensation reaction. The dynamic equilibrium between the two forms followed of azo-hydrozone tautomerism.

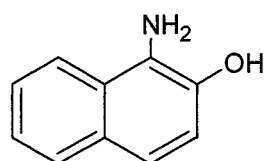
In many organic compounds, there is a mixture of two or more structurally distinct compounds to form rapid equilibrium this phenomenon called tautomerism that it is a Proton shifts from one atom of a molecule to a another molecule<sup>[107]</sup>. In the field of dyes, it is azo-hydrozone tautomerism such as the Scheme [1: 9]



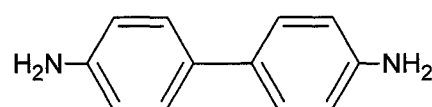
**Scheme [1: 9]**

### 1.2.6 Toxicity of dyes

In 1895 Rehn<sup>[108]</sup> showed that increased rates in bladder cancer in workers involved in dye manufacturing. After that time a lot of researches started showing the toxic potential of dyes these toxicity such as mortality, genotoxicity, mutagenicity and carcinogenicity and the most of these researches focused the effects of food colorants, usually azo compounds and dye manufacturing, azo dyes are primarily composed of aromatic amines, substituted benzene and naphthalene rings are common presence of azo dyes. Chung and Cerniglia in 1992<sup>[109]</sup> Reported that all the azo dyes containing a nitro group were found to be mutagenic, further, many of azo dyes when degradation can produce toxic products, for examples 1,4-phenylenediamine, 1-amino-2-naphthol, 2-Aminobiphenyl, 2-Naphthylamine, Benzedrine (prohibited) and substituted benzidines, such as o-tolidine. shows Figure 1.3<sup>[110]</sup>

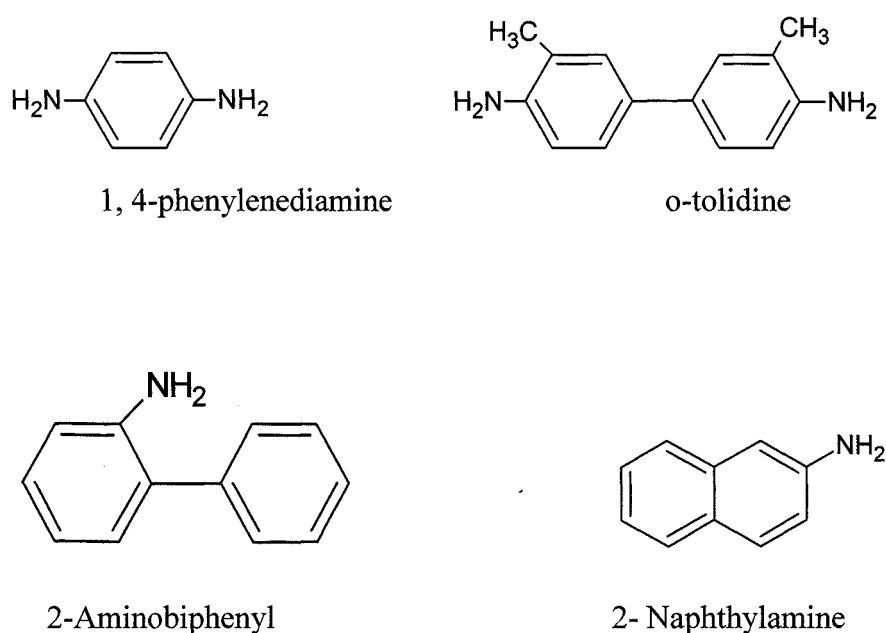


1-amino-2-naphthol



Benzedrine





**Figure1. 3 Chemical structures show toxic after metabolic activation of azo dyes.**

So azo dyes in purified form are Mutagenic or carcinogenic, only these dyes with free amino group consequently, reduction of azo dyes leads to formation of aromatic amines and several aromatic amines are known mutagens and carcinogens. The toxicity of aromatic amines depends on the structure of the molecule which means the location of the international agency for research on cancer(IARC) suspected most of them amino-sustituted azo dyes fat-soluble azo dyes and benzidine azo dyes some sulphonated azo dyes , many of these dye suspected from (IARC) list were taken out of production, also due to presence of heavy metals and salts in some dye at textile effluents this make complexed in the azo dyes these compounds can cause high electrolyte and conductivity concentrations in the dye wastewater, leading to toxicity problems.

the toxicity of dyes depends on the nature and location of the substituent's which means increase the toxicity with substitution nitro, methyl or methoxy groups or halogen atoms but lower toxicity with carboxyl or sulphonate groups

### **1.2.7 Decolouration**

About 70% of the Earth's surface is covered by water and there is great concern about contamination of these valuable resources. In Europe for example, the new Water Framework Directive seeks to achieve sustainable management of all water resources, ensuring that they meet a minimum quality status by a target date of 2015. Globally it is estimated that only 27% of the existing groundwater, lakes, rivers, polar ice and glaciers-can are adequately protected<sup>[111]</sup>. One of the most pollutants of water is dye, Dyes are considered to be particularly dangerous organic compounds for the environment; about 20% are left in the effluent during the dyeing process. some of them make serious health problems to human the major pollutants comes from textile industry and dye stuff manufacturing industry these pollutants are high suspended solids, chemical oxygen demand, heat, colour, acidity, and other soluble substance , as well as strong colour. The most dyes used in the textile industry are reactive dyes this due to bright colours, ease of application. The removal of dyes from industrial effluents is an area of research receiving increasing attention as government legislation on the release of contaminated.

#### **1.2.7.1 Methods of decolouration of dyes**

There are several factors that determine the technical and economic feasibility of each single dye removal technique these include composition of the waste water, dye type and cost of required chemicals each dye removal technique have its limitations and use of one individual method may not be sufficient to achieve complete decolourisation. The most important removal of hazardous dyes from textile effluent to support the economic and environmental sustainability of the industry<sup>[112]</sup>.the biological methods are cheap and simple to used, but can not be used to many wastewater because most commercial dyes are toxic to the organisms used in the process<sup>[113]</sup>. Traditional methods for treating textile dye waste waters such as coagulation and precipitation<sup>[114]</sup>, adsorption processes<sup>[115]</sup> with activated carbon, however, these processes may be costly, inefficient and often produce a high amount of secondary wastes , more advanced treatment process include electro coagulation technique<sup>[116]</sup> is considered to be potentially an effective tool for treatment of textile waste waters, Ultrasonic decomposition<sup>[117]</sup>, Uv

or combined oxidation processes<sup>[118]</sup>. The combined photochemical and biological processes<sup>[119]</sup>. Ozonation<sup>[120-123]</sup>, advanced chemical oxidation<sup>[124]</sup>, electrochemical oxidation<sup>[125, 126]</sup>, Fenton's reagent<sup>[127]</sup>, ozone and Fenton's reagent<sup>[128]</sup>, supported liquid membrane<sup>[129-131]</sup>, generally, the time needed for decoloration to occur varies from dye to dye which means impossible to make a general rule each method has advantages and disadvantages the most important methods is

## **1.2.7.2 Chemical decolouration methods**

### ***1.2.7.2.1 Oxidation Techniques***

Chemical oxidation is the most widely used techniques for the decolorization process in research and applied in industry, because that is due to diversity of chemical processes that can be effective these techniques include oxidation reactions, photochemical oxidations and electrochemical treatment. electrochemical technology has been applied to effectively remove acids as well as dispersed and metal complex dyes, Naumczyk, et al <sup>[132]</sup>, have been described the electrochemical techniques for the treatment of dye waste are more efficient than other treatments.

Chemical oxidation can be applied for one of several purposes in a wastewater treatment process depending on the results desired. These are

- treatment of toxic organics at low concentrations in groundwater,
- treatment of low volume-high strength waste-waters and enhanced biodegradability,
- treatment of waste-waters and normally subject to bio-oxidation e.g., cyanide and complex metals,
- Detoxification relative to aquatic toxicity following of biological treatment. Normally, some of biological treatment will be the most-effective technology for organic wastewater. Some organics, however, are either non-biodegradable or are toxic either to the biological process or to aquatic life and must therefore be pre or post treated.

The chemical oxidation is a very attractive technique for the purification of water contaminated with organic substances, especially with those, which are too toxic for

biological degradation. However, the direct reaction of organic molecules with oxygen, carried out at ambient temperatures, is usually too slow to be of practical use. Oxidation can be accelerated using high temperature as well as electric energy, but the application of these methods is not very extensive.

As environmental needs and regulations continue to become more severe through the 2000's, destructive treatment technologies consistent with waste minimization must be developed. Oxidation technologies are capable of achieving desired on site pollutant destruction and of hazardous wastes present a commercially viable alternative to meet these increasingly demanding needs. If carried out to its ultimate stage, oxidation can completely oxidize organic compounds to carbon dioxide, water and salts. Partial oxidation can result in increased biodegradability of pollutants so that; residual organic compounds can be removed through biological treatment. Many biological processes are, in fact, oxidative processes. or by bleaching, bleaching one of the best method for decolouration.

#### **1.2.7.2.2 Bleaching**

Bleaching has been defined as the structural modification of a coloured substance to give a colourless or less intensely coloured product. The process of bleaching can take place either in solution, or on the cloth. Bleaching agents range from oxygen, ozone, peroxides, chlorine and oxides of chlorine on one hand to sulphur dioxide and bisulphite ions on the other. The first method of bleaching used by Romans which was used sulphur dioxide fumes to bleach woollen goods and this method still used until the emergence of cheap hydrogen peroxide, bleaching by bisulphite( $\text{HSO}_3^-$ ) is the active species<sup>[133, 134]</sup>, there are disadvantages from using sulphur dioxide bleaching such that the substrate is reduced during bleaching and can be slowly oxidised back to its coloured form by aerobic oxygen. The numerous change in the textile industry after prepared bleaching powder (calcium hypochlorite) in eighteenth century because this bleaching powder is easy to use and store the solution very good bleaching medium for cellulosic fibres, then calcium hypochlorite replaced by sodium hypochlorite because there were no difficulties caused by the insolubility of residual unreacted hydroxide there are also disadvantages from using hypochlorite such as formation of highly toxic chlorinated organic by-products during the bleaching process, hydrogen peroxide is a weaker

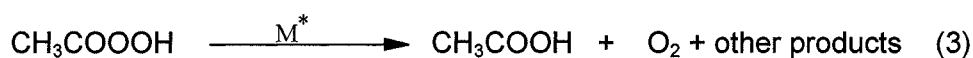
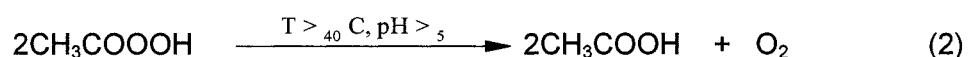
oxidising agent than hypochlorite and can be used to bleach polypeptide as well as cellulose fibres with much less risk of fibre damage.

Sodium perborate ( $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ ) and percarbonate ( $2\text{NaCO}_3 \cdot 3\text{H}_2\text{O}_2$ ) these two compounds used to produce hydrogen peroxide when dissolved in water, thus, can be used in domestic washing powders but require the high pH and high temperature to be effective.

An environmentally safe alternative to hypochlorite is peracetic acid at last few years, hypochlorite is being replaced by peracetic acid<sup>[135]</sup>, because PAA when it decomposes give oxygen and acetic acid this processes completely biodegradable, furthermore peracetic acid is higher brightness values with less fiber damage<sup>[135]</sup>, as well as better than hydrogen peroxide because that the a satisfactory degree of whiteness can be obtained at 60 °C in 40 minutes at neutral pH without the addition of auxiliary agents, at lower energy and water consumption when rinsing of the fabric,

there is also much less damage to the cotton fibre when peracetic acid is used<sup>[136-139]</sup>. the bleaching action of peracetic acid is mainly the result of epoxidation of the double

bonds present in unwanted coloured compounds the equations in Scheme [1:10] shows the mechanism of peracetic acid, hydrolysis, decomposition and oxidation<sup>[140]</sup>.



**Scheme [1: 10]**

#### 1.2.7.2.2.1 Mechanisms of bleaching

1. **Reductive Bleaching:** - such that action of sulphite on aromatic nitro compounds or bisulphite on carbonyl compounds could cause a decrease in

the length of the conjugated system accompanied by a shift towards the ultraviolet part of the spectrum. the reaction can often be reversed by aerobic oxidation of the bleached material

2. **Oxidative bleaching:** - generally involves disruption of the conjugated system of the coloured molecule-often going as far as the breakdown of the molecule into smaller fragments. The reaction can go via a free radical, electrophilic or nucleophilic attack on the substrate.

The synthetic organic chemicals that are being regulated to lower levels today are those which do not readily lend themselves to simple oxidative treatment. Depending on the nature of the oxidant, potentially hazardous by-products may be formed, e.g., chlorinated intermediates in chlorination processes. To minimize these by-products, uses of oxidants involving oxygen are being investigated. Oxygen itself is generally kinetically too slow to be practical, or requires severe conditions of temperature and/or pressure to effect complete oxidation. Active oxygen products, such as hydrogen peroxide and peracetic acid, are capable of providing the desired oxidation in many cases.

Other techniques are used recently for decolourization which called advanced oxidation process (AOPs). Are currently subject to a rapid evolution, especially those involving catalytic and/or photochemical systems, the successful application of AOPs depends primarily on the nature of the pollutants. Currently, only AOPs are considered to have the capacity for the complete elimination of the contamination. Complete oxidation, i.e. mineralization of organic pollutants. The most important in advanced oxidation process are briefly discussed in sections below.

### 1.2.8 Advanced oxidation process (AOPs)

In 1987, Glaze et al<sup>[141]</sup>, defined advanced oxidation processes as “near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radicals in sufficient quantity to effect water purification”.

Since the early 1970s advanced oxidation processes (AOPs) have been used to remove both low and high concentrations of organic compounds because the

treatment of waste water containing organic compounds like aromatic rings such as dyes , dyestuffs, chlorophenols by methods such as physical- chemical treatment(flocculation, precipitation and absorption) are not effective <sup>[142]</sup> or method such as traditional biotreatment<sup>[143, 144]</sup> in the advanced oxidation processes, the organic compounds can be completely converted to carbon dioxide and water mainly by hydroxyl radical<sup>[145, 146]</sup>. the hydroxyl radical which is the most powerful oxidizing agent generated ,this is due to ( $\bullet\text{OH}$ ) is acts very rapidly with most organic compounds, and this is as a results of oxidation and reduction which means transfer of one or more electrons from an electron donor (reductant) to an electron acceptor (oxidant) during to these processes from electron transfers producing chemical species with an odd number of valence electrons, these species called a radical and because one of their electrons is unpaired these species tend to be highly unstable and , thus ,highly reactive, so there are another oxidation reaction between the radical oxidants and other reactants until to reach stable oxidation products are formed to summarize above the advanced oxidation processes have two routs of oxidation (1) the formation of strong oxidants such as ( $\bullet\text{OH}$ ) (2) The reaction of these oxidants with organic contaminates in water. So the advanced oxidation processes is used to decompose many hazardous chemical compounds to acceptable levels, without producing addition hazardous by products or sludge which required further handling. Table1.5; - shows the relative oxidation power of some oxidizing species

Hydrogen peroxide is currently considered the most appropriate reactant for use in these technologies

**Table 1.5:- Relative oxidation power of some oxidizing species<sup>[147, 148]</sup>**

Oxidizing species	Relative oxidation power
Chlorine	1.00
Hypochlorous acid	1.10
Permanganate	1.24
Hydrogen peroxide	1.31
Ozone	1.52
Atomic oxygen	1.78
Hydroxyl radical	2.05
Positively charged hole on titanium dioxide, $TiO_2^+$	2.35

### 1.2.8.1 Methods generating •OH radicals

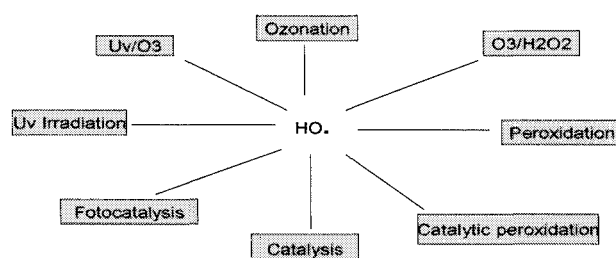
These involved photochemical and non- photochemical methods

Figure (1.4) shows the most popular techniques used recently for generation •OH to decolourization of dyes<sup>[149]</sup> is:-

Oxidation with Fenton's reagent ( $H_2O_2$  and  $Fe^{2+}$ ) photo catalysis and Ozonation ( $H_2O_2$  – Ozone), ( $H_2O_2$  – UV) radiation, Ozone / Ultraviolet Light ( $O_3$  /UV) ,  $H_2O_2$  / ozone / ultravioleta ( $H_2O_2$  / $O_3$  /UV), Photocatalytic oxidation (UV/  $TiO_2$  ) , $H_2O_2$  – peroxidise, peroxidise can also be used as hydrogen peroxide activator the efficiency of peroxidise

for the treatment is depends on the peroxidise used, concentration, pH, temperature of the medium. Thus, these techniques have been shown great potential for effectively removing dyes from waste water. These techniques based on the generation of highly reactive radical species, such as hydroxyl radical (•OH) which reacts with dye molecules<sup>[150]</sup> .the hydroxyl radical is a powerful oxidant and starts cascade of oxidation reactions that can in the end lead to total mineralization of organic pollutants .

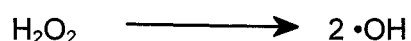




**Figure 1.4 Advanced oxidation processes<sup>[149]</sup>.**

### 1.2.8.2 H<sub>2</sub>O<sub>2</sub>-UV radiation

Hydrogen peroxide alone is ineffective to oxidization of the textile wastewater under both conditional acid and alkali values<sup>[151]</sup>. But under UV-irradiation H<sub>2</sub>O<sub>2</sub> are photolysied to produce two •OH radicals<sup>[76]</sup>.



thus hydrogen peroxide is activated by UV- light and there are many factors depending on treatment by H<sub>2</sub>O<sub>2</sub>-UV such as H<sub>2</sub>O<sub>2</sub> concentration in the intensity of UV- irradiation, pH, also dye structure . Shen Y.S. and Wang D.K. in 2002 <sup>[152]</sup> have been investigated the relationship between UV-light intensity and decomposition in Uv/H<sub>2</sub>O<sub>2</sub> process and found the decomposition rate of dye increase with increasing UV light intensity.

Shu et al <sup>[153]</sup> in 1995 have been found that acid dyes are that the easiest to decompose and the decolouration effectiveness decreases by increasing number of azo groups.

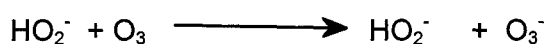
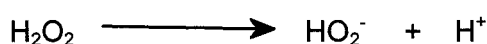
Pittroff <sup>[154]</sup> have been reported that the decolourisation is more rapidly at at reactive dyes and direct, metal-complex and disperse dyes but dyes have colour yellow and green reactive dyes is very slowly which means need longer reaction time.

### 1.2.8.3 Ozone, O<sub>3</sub> / UV

Rein M in 2001<sup>[155]</sup> have been found the Ozonation of organic compounds does not lead to oxidize organic to CO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> and they found the intermediate formation in some solution after oxidation maybe toxic or more toxic than initial compounds whereas the UV radiation could lead to complete the oxidation reaction by supplement the reaction with it. Hung-Yee in 1995 Reported that the ineffective decolorizing of dyes by UV or O<sub>3</sub> alone but the effective method of decolourizing of dye when combination of O<sub>3</sub> with UV (O<sub>3</sub>/UV). the efficient of ozone photolysis at UV radiation 254nm wavelength and can be formation Hydrogen peroxide as an intermediate, this lead to decomposes to •OH<sup>[76]</sup>.

### 1.2.8.4 H<sub>2</sub>O<sub>2</sub> -Ozone (peroxone)

The addition of both H<sub>2</sub>O<sub>2</sub> and ozone to wastewater accelerates the decomposition of ozone and enhances formation of the hydroxyl radical<sup>[76]</sup>.



Stachlin and Hoigne in 1982<sup>[77]</sup> have been reported that the reaction of H<sub>2</sub>O<sub>2</sub> with O<sub>3</sub> are very slowly at acidic pH, but more rapidly decomposition by H<sub>2</sub>O<sub>2</sub> at pH values above 5.

The combination of H<sub>2</sub>O<sub>2</sub> with two ozone molecules formation two •OH radicals.



Decolouration by this method is suitable for direct, metal-complex or blue disperse dyes<sup>[156]</sup>. But some problems with decolouration of acid dyes<sup>[156]</sup>.

More effective has been demonstrated when combined H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> process than H<sub>2</sub>O<sub>2</sub>/ or O<sub>3</sub> alone to remove pollutant and other synthetic organics, Therefore when combined H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> to produce hydroxyl radicals more than just O<sub>3</sub> which allows a lower dosage of O<sub>3</sub> to be used. This is desirable for reducing costs.

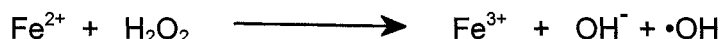
#### 1.2.8.5 Ozone – H<sub>2</sub>O<sub>2</sub> – UV-radiation (O<sub>3</sub>/ H<sub>2</sub>O<sub>2</sub>/Uv)

The efficiency of O<sub>3</sub>/ UV- system for accelerates the decomposition of zone, increased by addition of hydrogen peroxide to combine (O<sub>3</sub>/ H<sub>2</sub>O<sub>2</sub>/UV) the results increased rate of •OH generation<sup>[157]</sup>.

Azbar *et al.*, 2004<sup>[142]</sup> have been Reported that the most efficient for decolouration of dye house wastewater and polyester fiber dying process and acetate by combination of (H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/UV).

#### 1.2.8.6 Fenton system (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>)

Fenton,<sup>[158]</sup> have been discovered Fenton process from 1884 for maleic acid oxidation:



Fenton's reagent (hydrogen peroxide, activated by Fell salts is very applicable for the oxidation of wastewaters, this due to the rate constant for reaction of ferrous ion with H<sub>2</sub>O<sub>2</sub> is high and Fell oxidizes to FeIII very quickly even at excess amounts of H<sub>2</sub>O<sub>2</sub>.

The Fenton's system has the capacity to completely decolorize and partially mineralize textile industry dyes in short reaction time, as documented by some studies<sup>[137, 139, 159]</sup>.

The main advantages of use (Fe<sup>2+</sup>/ H<sub>2</sub>O<sub>2</sub>) as an oxidant iron is a highly abundant and non-toxic element and the H<sub>2</sub>O<sub>2</sub> is easy to handle and environmentally benign.

Also Fe(III) – oxalate complexes were used as a kind of catalyst in the photodegradation of textile dyes in water<sup>[160-162]</sup>.

#### 1.2.8.7 Photocatalytic oxidation (Uv/TiO<sub>2</sub>)

One of the most widely used metal oxides in industry is Titanium dioxide, both in the forms of anatase and rutile also its use as a catalyst support or as a catalyst

and photocatalyst it self. the  $\text{TiO}_2$  as photocatalyst is one of the most advanced oxidation processes used recent years, the basis of photocatalysis is the photo-excitation of a semiconductor that is solid as a result of the absorption of electromagnetic radiation, as,  $\text{TiO}_2$  is illuminated by light with wave length less than 380nm, the photons excite valence band electrons a cross the band gap in the conduction band, then leaving holes behind in the valence band. After that the holes in  $\text{TiO}_2$  react with water molecules or with hydroxide ions to produce  $\bullet\text{OH}$  radicals, therefore generation of hydroxyl radicals depends on the solution pH.

There are many studies has been investigated the dye by photocatalytic oxidation and amenable to oxidize a wide variety of toxic and organic compounds to harmless e.g carbon dioxide and water <sup>[163]</sup>.

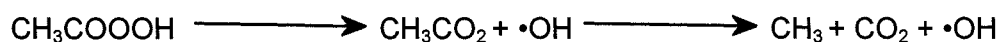
in furthermore titanium dioxide interacts with the supported phase as a promoter <sup>[164]</sup>. This technique are used to the interaction between chloride ions and  $\bullet\text{OH}$  radicals in photocatalytic treatment of reactive dye based on  $\text{TiO}_2$ , the chloride ions could react with  $\bullet\text{OH}$  radicals and reduce the amount of  $\bullet\text{OH}$  radicals a available for the oxidation reaction.

### 1.2.9 Reduction processes.

Reduction processes are also widely used for the decolourization of dyes.

We have seen from all of these processes can produce hydroxyl radicals, which can react with and destroy a wide range of organic contaminants.

Also peracetic acid might be a convenient source of  $\bullet\text{OH}$  hydroxyl radicals both in the gas phase and in solution, the radicals being formed by sequence of reactions <sup>[165]</sup>.



The second order rate constant of oxidation of the organics with hydroxyl radicals range from  $10^8$  to  $10^{11} \text{ M}^{-1} \text{ S}^{-1}$  and the reaction rate constants of molecular ozone with different organic compounds are also given in Table (1.6).

**Table 1.6 Reaction rate constants ( $k$ ,  $M^{-1} s^{-1}$ ) of ozone vs. hydroxyl radical <sup>[166]</sup>**

Compound	O <sub>3</sub>	•OH
Chlorinated alkenes	$10^3-10^4$	$10^9-10^{11}$
Phenols	$10^3$	$10^9-10^{10}$
N-containing organics	$1-10^2$	$10^8-10^{10}$
Aromatics	$1-10^2$	$10^8-10^{10}$
Ketones	1	$10^9-10^{10}$
Alcohols	$10^{-2}-1$	$10^8-10^9$

### 1.2.10 Disadvantages of advanced oxidation Process

There are disadvantages to AOPs under certain circumstances. For example: ozone must be produced on site, and is expensive; the Fenton system, using hydrogen peroxide and ferrous ions produces a lot of ferric sludge, and the pH<sup>[167]</sup> of the system must be strictly controlled by the addition of mineral aids such as sulphuric acid; and UV irradiation is ineffective in soil matrices or strongly absorbing solutions. There is, moreover, a fundamental problem with AOPs in circumstances where biorefractory pollutants are mixed with easily degradable ones, or with natural organic compounds from the breakdown of living organisms. The very strength of AOPs is the production of hydroxyl radicals that are strong and indiscriminate oxidants. In mixed pollutant environments the oxidising power is wasted on chemicals that are harmless or easily degraded by natural processes. A profound weakness of the Fenton (hydrogen peroxide-ferrous) system is that a rapid burst of hydroxyl radical is produced, so that in dilute solutions of pollutants most of the oxidising power of the peroxide is dissipated in wasteful O<sub>2</sub> production via superoxide, HOO formed from the reaction of hydroxyl radicals and hydrogen peroxide.

### **1.2.11 Physical methods of decolouration**

There are several known methods these included traditional physical- chemical techniques (ultrafiltration, reverse osmosis, ion exchange, coagulation- flocculation and adsorption),

#### **1.2.11.1 Ultrafiltration**

Ultrafiltration which means filtration with bigger pores this technique is suitable as pre-treatment<sup>[168]</sup> or in combination with a biological reactor<sup>[169]</sup>, but is generally not successful as the membrane pore size is too large to prevent dye molecules from passing through.

#### **1.2.11.2 Coagulation- flocculation**

coagulation- flocculation treatments are generally used to eliminate organic substances, but the chemicals normally used in this process have no effect on the elimination of soluble dyestuffs, but effectively eliminates insoluble dyes<sup>[170]</sup>

the technique of coagulation-flocculation is based on the addition of a coagulant followed by a generally rapid association between the coagulant and the pollutants, then produce coagulates or flocks subsequently precipitated are then removed by either flotation, by further treated to reduce its water content and toxicity<sup>[171, 172]</sup>

the last few years have been developed organic anionic, cationic or non- ionic coagulant polymers rather than inorganic coagulants( aluminium, magnesium, calcium and iron salts), for colour removal treatments, in addition they offer advantages over inorganics such as lower toxicity and improved colour removal ability and lower sludge production<sup>[173, 174]</sup>

#### **1.2.11.3 Adsorption**

The main abiotic mechanism for removing dyes from the wastewaters is adsorption on sludge quality and this technique is more popular because of great efficiency in the removal of pollutants too stable for conventional methods. Activated carbon is the most used method of dye decolorization by adsorption, to contrast with peat, fly

ash, and coal, wood chips and corncob and is very effective for adsorbing cationic, mordant and acid dyes<sup>[175, 176]</sup>.

The second adsorbent, suitable for wastewater treatment called biomass

Biomass decolorization of azo dye is a result of two mechanisms adsorption into solid matrix and ion exchange which depends on the dye molecule size and charge, pH of medium and salt concentration.

The main disadvantage of adsorption processes needs to be regenerated this led to increase the cost of the process.

### **1.2.12 Biological degradation**

Biological degradation or breakdown by living organisms

The most important removal process of organics biological degradation or breakdown by living organisms which means are transferred from industry processes into solid and aquatic ecosystems, biological degradation are different depending on the presence or absence of oxygen<sup>[177]</sup>, there are a wide range of micro-organisms including bacteria, fungi, and algae are capable of efficiently decolourising a wide range of dyes also used

Anaerobic-aerobic (combined) biodegradation there is a complete decolourisation of dyes and significant reduction in BOD and COD levels. The most important of biological degradation is bacteria and fungi.

#### **1.2.12.1 Bacterial**

There are variety of studied has been investigated that the ability for both bacteria to metabolize and bacteria with specialized reducing enzymes to aerobically degradation of certain azo dyes<sup>[178-180]</sup>, at aerobic conditions azo dyes are not readily metabolized but under anaerobic conditions many bacteria reduce azo dyes by the activity of unspecific, soluble, cytoplasmatic reductase.

The first step in the biodegradation of azo dye reduction resulting in the formation of the aromatic amines<sup>[181]</sup> and these aromatic amines some times toxic, mutagenic<sup>[182]</sup>. it is necessary to another step to achieve complete degradation of azo dye to avoid toxicity of dyes and this steps involves aerobic biodegradation<sup>[183]</sup>, therefore biological treatment strategy based on anaerobic

reduction of the azo dyes, followed by aerobic transformation of the formed aromatic amines.

In non azo dyes such as aerobic decolourization of triphenylmethane dyes<sup>[184]</sup>, bacterial biodegradation can be degradation of anthraquinone dyes<sup>[185]</sup>, under anaerobic conditions can be degradation of phtalocyanine dyes<sup>[186]</sup>.

#### **1.2.12.2 Fungal**

The use ligninolytic fungi is one of the possible alternatives studied for the biodegradation of dyes, fungi is responsible for the decolorization and degradation of a number of dyes<sup>[182]</sup>. White-rot fungi in particular produced enzymes as lignin peroxidise, manganese peroxidise that degradation of many aromatic compounds due to their non- specific activity<sup>[180]</sup>.

#### **1.2.13 advantages and disadvantages of methods of dyes**

The table 1.7 shows advantage and disadvantages of some methods of dyes removal from wastewater.



**Table 1.7:- The advantages and disadvantages of some methods of dyes removal from wastewater. Adapted from <sup>[187]</sup>.**

Method	Advantages	Disadvantages
Adsorption	low cost no regeneration needed dye-adsorbed materials can be used as substrates in solid state fermentation	some adsorbents have low surface area possible side reactions loss of adsorbents performance depends on wastewater characteristics
Nanofiltration	removes all dye types high effluent quality easy to scale-up	high investment costs membrane fouling effluent must be treated
Electro coagulation	removes small colloidal articles no use of coagulants low sludge production low cost	not effective for all dyes
Coagulation and perception	effective for all dyes	high cost high sludge production
Advanced chemical oxidation	non-hazardous end products	high cost
Electrochemical oxidation	no sludge production breakdown compounds are non-hazardous no chemicals used	high cost
Photo oxidation	no sludge production	releases aromatic amines
Ozonation	no sludge production no alteration of volume	high cost short half life
Supported liquid membrane	minimal loss of extractants simple to operate low energy consumption easy to scale up low cost	emulsification may occur
Liquid-liquid extraction	low cost low energy consumption variety of solvents available easy to scale-up	emulsification may occur effluent must be treated
Biological processes	environmentally friendly public acceptance economically attractive	slow process needs adequate nutrients narrow operating temperature range

### 1.3 Aims of this project

The research programme aims to compare existing advanced oxidation process (AOPs) with new approaches that either depends on the formation of alternative peroxide species from hydrogen peroxide or which use less extreme conditions of pH than are necessary for the Fenton reaction. The kinetics and equilibria of peracid formation from hydrogen peroxide and parent carboxylic acids will be studied under a range of aqueous conditions with a variety of catalysts. The properties of the resulting equilibrium mixture will be investigated in terms of its reactivity toward model pollutant substrates. For certain reactions it is known that the ferrous ion catalysed reactions with peracetic acid are faster than the corresponding reactions with Fenton's reagent<sup>[188]</sup>. The effects of catalysts, light, and other perturbations on the reactivity of the equilibrium mixture are assessed and compared with their effects on the reactivity of hydrogen peroxide alone under comparable conditions.

Davies and co-workers have carried out a number of studies of peroxide bleach activators, where peracids and acyl peroxides are formed via acyl transfer from an ester or amide activator molecule to hydrogen peroxide<sup>[189]</sup>. Peracids are much more powerful oxidants than hydrogen peroxide but much more specific oxidants than hydroxyl radicals. The use of activator molecules to form peracids vastly reduces the atom efficiency of the process in Green Chemical terms. Alternatively, peracids can be prepared directly from the reaction of hydrogen peroxide and the parent carboxylic acid at low pH. The reaction of acetic acid and hydrogen peroxide in dioxin, for example, has an equilibrium constant  $\frac{[\text{peracetic acid}][\text{H}_2\text{O}]}{[\text{acetic acid}][\text{H}_2\text{O}_2]}$  about 0.8, and is acid catalysed[18]. This extrapolates to an equilibrium constant  $\frac{[\text{peracetic acid}]}{[\text{acetic acid}][\text{H}_2\text{O}_2]}$  of about  $0.015 \text{ M}^{-1}$  in water. ( $[\text{H}_2\text{O}] = 55 \text{ M}$  in water). The equilibrium constant should be independent of pH up to the pKa of acetic acid, 4.7, and thereafter drop with decreasing  $[\text{H}^+]$  until pH 8.2, the pKa of peracetic acid, where it will level out at about  $5 \times 10^{-6} \text{ M}^{-1}$ . When peracids oxidise organic compounds the parent carboxylic acid is often regenerated and so, under appropriate conditions, simple biodegradable carboxylic acids can act as catalysts for the reactions of hydrogen peroxide.

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## **Peroxide reactions of environmental relevance in aqueous solution**



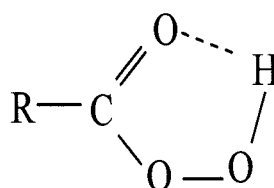
# Chapter 1

## General introduction

### 1.1 Peroxoacid

#### 1.1.1 The chemistry of peroxoacid

Organic peroxy acids are one of the most useful classes of organic peroxides due to the wide range of specific oxidation reactions that they perform, which are always high in quantitative yield. Organic peroxy acids, or peracids, are derivatives of hydrogen peroxide in which one of the hydrogen atoms is replaced by an acyl or aroyl group monoperoxy acids containing one peroxy carboxyl(-CO<sub>3</sub>H) group; diperoxy acids contain two. No examples of tri-or higher peroxy acids are known.



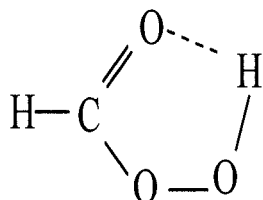
Structure [1:1]

Both dipole moment measurements of aliphatic peroxoacid<sup>[1]</sup>, and infra red spectral evidence<sup>[2]</sup>, reported that peroxoacid have, to a greater or lesser extent, a skew have been conformation about that the O - O bond in peroxides is similar to that shown in hydrogen peroxide.

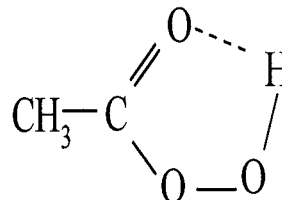
The U.V. spectra of peroxoacid are in the same way to those hydrogen peroxides, which means they exhibit a continuously increasing absorption as the wavelength decreases. In 1962 Symons has been concluded that for hydrogen peroxide the oxygen lone pair electrons or electrons in weakly "pi" ant bonding orbital's at the transitions<sup>[3]</sup>.

### 1.1.2 The systematic name

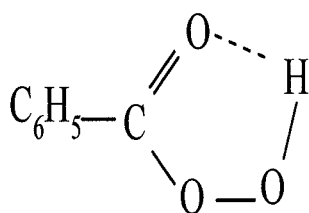
The word peracids has been in common use from long time ago and many works still use it. The systematic name, which clearly indicates the presence of peroxide oxygen in the molecule and avoids ambiguity in certain cases, is preferred.



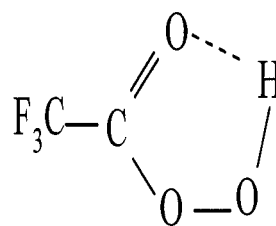
Peroxyformic acid (performic acid)



Peroxyacetic acid (peracetic acid)



Peroxybenzoic acid (perbenzoic acid)



Peroxytrifluoroacetic acid  
(Trifluoroperacetic acid)

Figure 1.1; - some typical examples of organic peroxy acids

### 1.1.3 Peroxoacid and pKa

Parent acids are generally stronger acids than the Peroxoacid. Some examples are listed below shows the pK of the acids and their respective peracids.

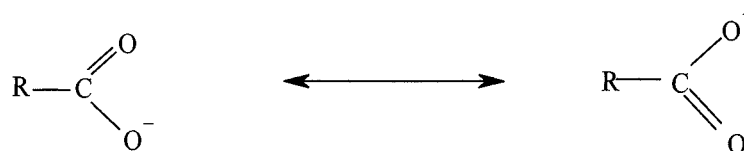
Table 1.1:- shows the peroxxoacid with pKa <sup>[4]</sup>.

	pK		pKa
Formic acid	3.8	Performic acid	7.1
Acetic acid	4.7	Peracetic acid	8.2
Propionic acid	4.9	Perpropionic acid	8.1
Sulphuric acid	1.9	Peroxomonosulphuric acid	3-4

For example, peracetic acid has a pKa of 8.2 <sup>[5]</sup>, whereas acetic acid has a pKa of 4.7. There are two explanations for this.

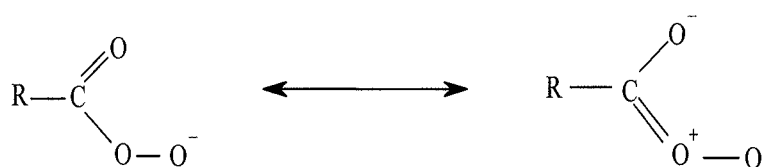
One explanation is that intermolecular hydrogen bonding stabilizes the neutral molecule relative to the anion form<sup>[6]</sup> such as structure [1:1]

The second explanation is that the parent carboxylic acid has an anion form stabilized by a delocalized electronic configuration <sup>[7]</sup>. Scheme [1:1]



*Scheme [1:1]*

Whereas canonical resonance forms would be much less likely to contribute to the peroxyanion ground state <sup>[7]</sup>.scheme [1:2]



*Scheme [1: 2]*

Moreover, the methyl substitutions in alkyl hydroperoxides and aryl substituents in Peroxybenzoic acids affect the pKa values less than in the parent of alcohols and benzoic acids respectively. This is due to that polar and electronic effects is weakened in passing through the O – O bond to affect the strength of the terminal O –H bond <sup>[5]</sup>

Since the O – O link is one atom longer and electronically saturated so this weakening of the electronic effect is not unexpected. There are other weakening is

observed in organic systems by insertion of a methylene group between substituent and reaction site.

The dissociation constants of peroxomonosulphuric acid<sup>[8]</sup> and peroxomonophosphoric acid<sup>[9]</sup> have been measured spectrophotometrically utilizing the increase in extinction in the ultra violet region on ionization of the peroxidic proton.

Due to the decomposition of the peroxyacid during the titration it is cannot be measurement of dissociation constants to a high degree of accuracy.

## 1.1.4 Peroxyacid decomposition

### 1.1.4.1 Auto decomposition

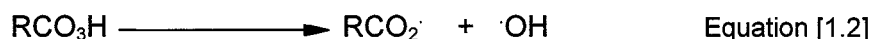
Organic peracids decompose spontaneously auto decomposition to produce parent acids and oxygen, The rate of decomposition,  $v$ , is maximised at the  $pK_a$ <sup>[10]</sup>. as can be seen in this equation.



### 1.1.4.2 Effect of thermolysis and photolysis

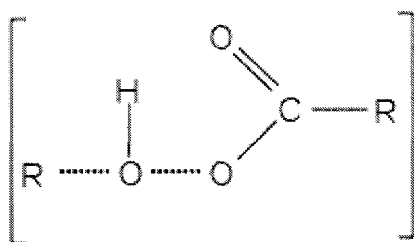
The thermal decomposition of peroxyacetic acid has been studied in both the vapour phase<sup>[11]</sup>, and in aromatic solvents<sup>[12]</sup>. Under these conditions the decomposition is mainly homolytic and the dissociation energy of the O-O bond has been reported from activation energies to be 30 to 34 k cal mole<sup>-1</sup>.

Leffort et al<sup>[13]</sup>. has been demonstrated systematically the radical decomposition of peroxyacids by thermolysis, Ando<sup>[14]</sup> have been give the most important facts for these reactions below.





Rapidly decarboxylation of the carboxy radicals in equation [1.3]. The relative reactivities of radicals with peroxyacids [1.4] correlate with their ionisation potentials, they are explained by the following polar effect in structure [1.2]

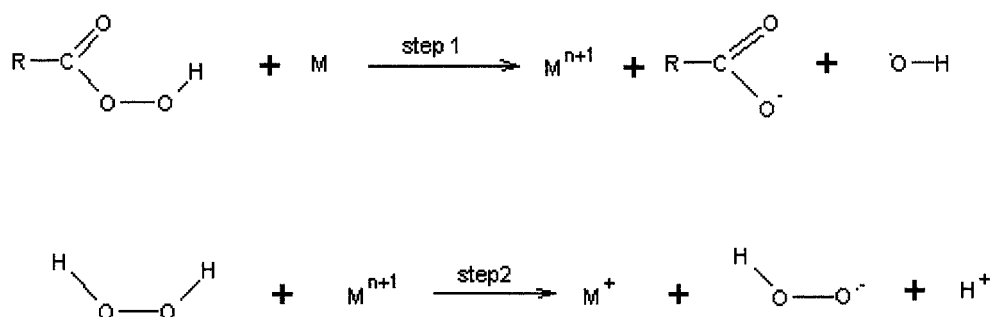


Structure [1:2]

### 1.1.4.3 Metal ion interactions

Decomposition of peroxyacid has been shown to take place in aqueous solution via free radical pathway when catalysed by metal ions of variable valence<sup>[15]</sup>.

Scheme [1: 3] below shows that hydrogen peroxide able to the catalysis of metal ion decomposition, where M is the metal ion of variable valence.



**Scheme [1: 3]:- Peroxide synergism in redox cycling with metal ions**

Ethylenediaminetetraacetic acid(EDTA), has been shown to drastically reduce the metal catalysed decomposition of peroxyacid and hydrogen peroxide<sup>[15, 16]</sup>.

Presumably by sequestering the trace metal ions, and has been used in a number of researches to reduce metal catalysed reaction.

The reaction shown in scheme [1.3] is not suppressed by Ethylene diaminetetraacetic at high pH. The discovery that polyaminopolphosphonates inhibited peroxide loss because of suspicion of radical involvement in the reaction mechanisms <sup>[17]</sup>.

### 1.1.5 The Preparation of peroxyacid

Numerous methods are known for the preparation of peroxyacids, some are general while other is specific for certain peroxyacids only these preparations are summarized in table (1.2) below.

**Table1.2:- summary of types of reaction that have been reported for preparing peroxyacids.**

	Reference
$\text{RCO}_2\text{H} + \text{H}_2\text{O}_2 \text{ (30 to 98\%)} \xrightleftharpoons{\text{H}^+} \text{RCO}_3\text{H} + \text{H}_2\text{O}$	[18-20]
$\text{RCHO} + \text{O}_2 \xrightarrow{\text{free radical chain reaction}} \text{RCO}_3\text{H}$	[21-23]
$\text{RCO}_3\text{COR} \xrightarrow{\text{Hydrolysis}} \text{RCO}_3\text{H} + \text{RCO}_2\text{H}$	[24, 25]
$\text{RCO}_2\text{COR} + \text{H}_2\text{O}_2 \longrightarrow \text{RCO}_3\text{H} + \text{RCO}_2\text{H}$	[18, 26, 27]
$\text{RCOCL} + \text{H}_2\text{O}_2 \xrightarrow{\text{base}} \text{RCO}_3\text{H} + \text{HCL}$	[18, 28, 29]
$\text{B (OCOR)}_3 + 3\text{H}_2\text{O}_2 \longrightarrow 3\text{RCO}_3\text{H} + \text{H}_3\text{BO}_3$	[18, 30]

By carefully mixing the hydrogen peroxide and carboxylic acids in the presence of an acid catalyst such as sulphuric acid, the most effective and a majority commonly used as a catalyst is the sulphuric acid or sulfonic acid type ion-exchange resins, but other acids can be used.

From table 1.2 we can see that reaction 1 is reversible, and the conversion and yields of peroxy acids are highest when the water content is at a minimum. This is accomplished either by the use more concentrated hydrogen peroxide<sup>[31]</sup>, or the use of excess aliphatic acid.

Peroxyacetic acid it is one the oldest know peroxy acids and have been prepared from long time ago 1864 by mixed diacetyl peroxide with Brodie<sup>[32]</sup>, but it was not isolated and characterized until much later in the classical work of D'Ans and his co-workers<sup>[33]</sup>.

The most important and widely used peroxy acid is the Peroxyacetic acid, there fore the number of publications and patents describing its properties, preparation and reactions.

In the early 1900s the first dilute aqueous solutions of Peroxyacetic acid were obtained by the mild hydrolysis of diacetyl peroxide<sup>[34],[35]</sup>, and of benzoylactyl peroxide<sup>[36]</sup> due to the reaction of diacetyl peroxide with dilute aqueous hydrogen peroxide<sup>[37]</sup> or by the reaction of diacetyl peroxide with base followed by acidification. In 1945 the reaction of acetic an hydride with an inorganic peroxide or with dilute solution of hydrogen peroxide has been used to obtain dilute solutions of Peroxyacetic acid or its salts<sup>[38]</sup>.

#### **1.1.5.1 Direct Preparation from acetic acid**

Reaction 1, table 1.2 shows that the direct acid catalyzed reaction of 30 to 98% hydrogen peroxide with acetic acid to preparation of peroxy acetic, this method was the most important and widely used to preparation of Peroxyacetic acid, the acid catalyzed formation and hydrolysis of peroxy acetic acid is bimolecular and involves acyl-oxygen cleavage<sup>[39]</sup>.the specific reaction rate constant at the formation of Peroxyacetic acid from acetic acid and hydrogen peroxide is reported to be  $7.4 \times 10^{-6}$

liters mole<sup>-1</sup> sec<sup>-1</sup> this is at temperature 25°C<sup>[40]</sup>, in the presence of 2% by weight of sulphuric acid.

Pungor and co-workers<sup>[41]</sup> have been published the rate constants at higher reaction temperatures and at varying hydrogen peroxide concentration and water. Sulphuric acid as well as has been used as a solvent reaction medium for preparing peroxy acetic acid<sup>[42-44]</sup>. But the disadvantage have been seen from using large quantities of sulphuric acid with carboxylic leads to miscible with hydrogen peroxide, for this reason the use of more sulphuric acid or other catalysts such as nitric, hydrofluoric, and phosphoric acids than is need to speed up peroxy acid formation is unnecessary complication.

The equilibrium constant for the preparation of Peroxyacetic acid from acetic acid and hydrogen peroxide is somewhat uncertain. Values ranging from approximately 3<sup>[45]</sup> to 7<sup>[33]</sup> have been reported in the temperature range 0 to 25°C. The main three effects that related to the equilibrium constant for Peroxyacetic acid formation is sulphuric acid hydrogen peroxide concentration and temperature<sup>[46],[47]</sup>. As anhydrous conditions are approached, the equilibrium constant is reported to increase to approximately 4.5 at 25°C<sup>[47]</sup>. The variation in values has been attributed to analytical difficulties and decomposition with loss of active oxygen. In 1965 Sawaki and Ogata<sup>[48]</sup> has been confirmed that the increase in the concentration of sulphuric acid leads to increase in equilibrium constant (K).

### **1.1.6 The electrophilic of peroxyacid**

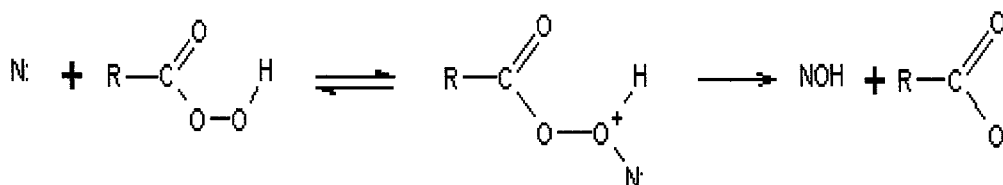
Peroxyacid are ambident electrophiles and attack either takes places at the outer peroxides oxygen or at carbonyl carbon.

#### **1.1.6.1 The outer peroxidic oxygen**

The outer peroxidic oxygen has non bonded electrons and reacts faster with polarisable Soft nucleophiles it is reacts much faster with Iodide than chloride<sup>[49]</sup>. The electrophilic oxidation of azobenzene by peroxobenzoic acid in benzene produces azoxybenzene. The second order rate constant is  $2.31 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ . the rate increases with electron donating substituents on the azobenzene<sup>[50]</sup>.



As there is many reducing agents are nucleophiles, oxidation may take place by displacement mechanism on the oxygen ,in 1962 Edwards<sup>[51]</sup> proposed A simple model for the transition state see Scheme [1: 4] below.



**Scheme [1: 4]:- A simple model for transition state**

From this model there are many predications are possible such as;-

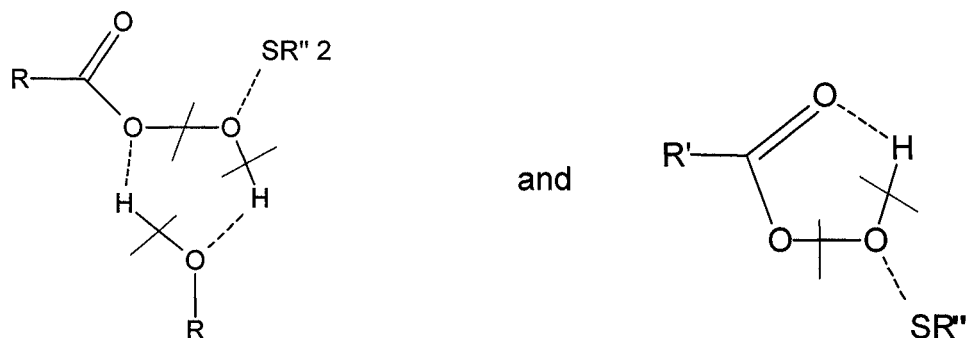
- The entropy of activation should be negative.
- Less basic leaving groups  $\text{RCOO}^-$  should increase.
- Since there is unshared electron pair on the oxygen atoms various types of acid catalysis should be apparent.

The above properties have shown in acidic solutions when oxidations of halides such as the oxidations of chloride and bromide ions by peroxyacetic, peroxomonosulphuric acids<sup>[49]</sup> or iodide by substituted peroxobenzoic acids<sup>[52]</sup>.

The slopes of the plots of log second order rate constant against the pKa of the parent acid are -0.5 the electron withdrawing groups increase the rate. The magnitude of the effect is less than is generally the case but consistent with results produced for other hydroperoxides and halide ions<sup>[51]</sup>.

In reactions such as the oxidation of Olefins to epoxides and sulphides to Sulphoxides the scheme suggested by Edwards above is even less satisfactory energetically than in the case of halides or other negatively charged nucleophiles since it involves charge separation in going from reactants to products.

In 1970 Edwards<sup>[53]</sup> proposed that these reactions are influenced by solvation of the ground state both of the substrate and peroxyacid also the transition state. And proposed structures, Scheme [1: 5], for the transition state in both protic and aprotic solvents which involve by passing of charge separation.

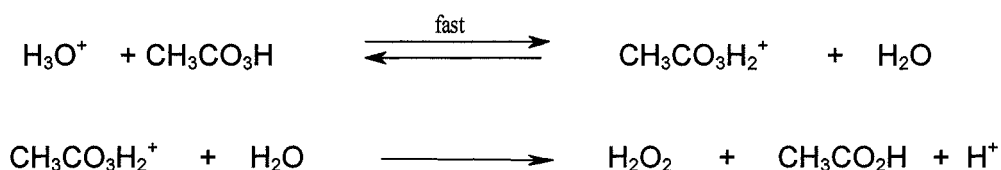


**Scheme [1: 5]:- the transition state in both protic and aprotic solvents.**

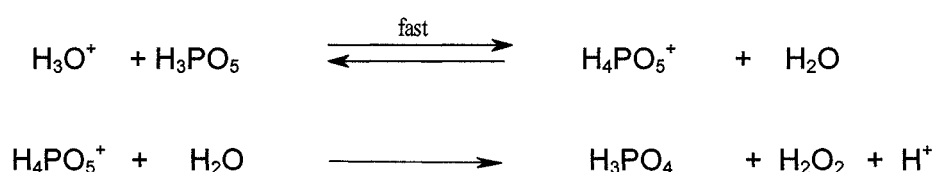
There are many studies shows the transition states is similar to those suggested by Edwards such as oxidation of sulphines to ketones<sup>[54]</sup> and acetylenes<sup>[55]</sup>.

### 1.1.6.2 The carbonyl carbon in peroxy acids

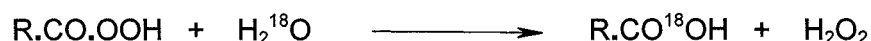
The carbonyl carbon is relatively *hard* since it has some positively charged character. It reacts with hard charged non – polarisable bases such as hydroxide. The transition state consisted of nucleophilic attack of water on the conjugate acid of the peroxyacetic acid in 1956 Bunton<sup>[56]</sup> studied the hydrolysis of peroxyacetic acid and found it to be acid catalysed.



The similar conclusion for the hydrolysis of peroxomonophosphoric acid have been reported by Battaglia and Edwards<sup>[9]</sup> and they suggested the possibility of a non acid catalysed pathway but under the conditions necessary to measure this the decomposition of the peroxyacid was the predominant reaction.



By using an  $^{18}\text{O}$  isotope label<sup>[56]</sup> and the mechanisms proposed for the peracetic acid synthesis and hydrolysis it has been shown that<sup>[48, 57, 58]</sup> the reaction did not involve dissociation of the O-O bond in the initial hydrogen peroxide, Bunton et al in 1956 was proved conclusively using  $\text{H}_2^{18}\text{O}$  as solvent that hydrolysis involves cleavage of the carbon-oxygen bond, this means that the acyl group and oxygen atom is cleaved in both of the formation and hydrolysis of peroxyacids



### 1.1.7 Oxidation Capacity of Selected Sanitizers

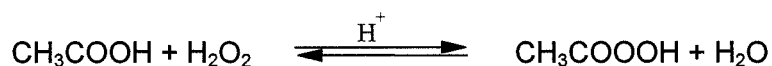
The peracetic acid is stronger oxidizer and have a higher oxidation potential more than chlorine dioxide and sodium hypochlorite but less than ozone, therefore the peracids inactivates which that responsible for degradation, the table(1.3) below shows that the oxidation capacity of peracids.

**Table1.3 :- shows the oxidation Capacity of Selected Sanitizers.**

Sanitizer	eV*
Ozone	2.07
Peracetic Acid	1.81
Chlorine dioxide	1.57
Sodium hypochlorite (chlorine bleach)	1.36

### 1.1.8 Peroxide determination Techniques

Peracetic acid is a strong oxidizer most analytical techniques for peracetic acid are based on the redox properties of the acid. This is due to the acid-catalysed equilibrium shows equation below,

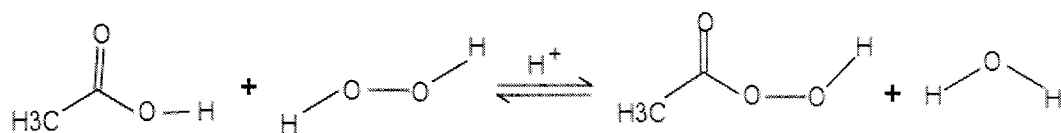


Hydrogen peroxide is always present in peracetic acid solution this is because of the peracetic acid is technically synthesized by mixing concentration solution of acetic acid and hydrogen peroxide in the presence of sulphuric acid as catalyst. The quantitative determination of peracids is difficult, because watery peracids solutions always contain hydrogen peroxide, which shows similar reactions. So hydrogen peroxide and peracids are high reactive oxidising agents and have similar reactivities with many reagents used in peroxide determination making resolution of a mixture of these peroxides difficult. for example the uncatalyzed reaction of peracetic acid and  $I^-$  is by 5 orders of magnitude large than of hydrogen peroxide with  $I^-$  <sup>[59]</sup>. Therefore, the development of a fast and reliable method for the determination of PAA in aqueous solutions is of great interest.

Various methods have been reported for the determination of peracetic acid in acidic solution, the most widely used methods for analyzing solution containing peracetic acid and hydrogen peroxide are ,Titration methods by D'Ans and Frey<sup>[60]</sup> and its modification by Greenspan and Mckellar<sup>[61]</sup> , and this method utilized by sully and Williams<sup>[62]</sup>.

Conductivity measurements, photometry <sup>[63-66]</sup>. Spectrophotometry <sup>[67-69]</sup> . gas and liquid chromatography determination <sup>[70-73]</sup>. Electrochemical sensors measurements<sup>[74-77]</sup>.

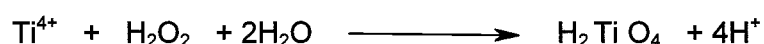
D'Ans and Frey<sup>[60]</sup> have been described methods for the analysing solution containing peracetic acid and hydrogen peroxide .in this method the hydrogen peroxide is first titrated with permanganate and then adding potassium iodide to determined the peracetic acid with titration the liberated iodine with thiosulphate.



**Scheme [1: 6]:- Acid- catalysed equilibrium**

In 1948 Greenspan and Mackellar <sup>[61]</sup> have been utilized a similar method to determine peracetic acid in the presence of hydrogen peroxide, which first titrating the hydrogen peroxide with ceric sulphate(IV) (ammonium tetra sulfatocerate), followed by an iodometric determination of the residual peracetic acid present and this method utilized by sully and Williams <sup>[62]</sup> to avoid significant equilibration of the peroxide in the acidic conditions the titrations must be carried out rapidly with temperature below 10<sup>0</sup> C <sup>[62]</sup> and much greater reactivity of iodide with peracetic acid than with hydrogen peroxide Therefore, liberated iodine by titrated with 0.1N sodium thiosulphate this was repeated several times about 10 minutes by plotting titration versus time and extrapolating back to zero time to obtained the corrected titre corresponding to the peracetic acid present and calculate hydrogen peroxide from total titration this method is widely used to resolve solution containing peracetic acid and hydrogen peroxide consequently, the reliability of this method is gives very good results when concentrations of the two peroxo species are comparable,

In 1943 Eisenberg have described<sup>[78]</sup> a Colorimetric method for the determination of low levels of hydrogen peroxide concentration as low as 5.29x10<sup>-5</sup> M involves reaction with acidified, which utilizes the yellow coloured complex produced between the titanium (IV) ion and hydrogen peroxide with maximum absorption at 400nm according to the reaction below



The complex of Titanium is often written as  $\text{TiO}_2^{2+}$  <sup>[79]</sup> the titanium (IV) complex methodis selective for hydrogen peroxide at room temperature, at high temperature the colour development is proportional to the total peroxide concentration in a solution<sup>[80]</sup>. Ogleby and Williams<sup>[80]</sup> has been applied to use this property to measure concentration of amixed solution from peracetic acid and hydrogen peroxide (approximately 15% PAA, 14%  $\text{H}_2\text{O}_2$ ) the solution will be divided into samples one heated to (90-95 c) and second one cold which remains at room temperature, then the titanium (IV) oxide assay reagent is added simultaneously and the colour development in the two samples compared, allowing the calculation of the respective percentages of the two peroxides which means the colour development, The colour development in the two pairs, the colour developed in the pair without

heating is proportional to the hydrogen peroxide content of the sample but the colour developed in the pair heated is proportional to the total peroxide content in the sample the resulting difference signal from the colorimeter is proportional to the peracetic acid content of the sample this method measuring peracetic acid in the range 1-500mg L<sup>-1</sup> .in practice , in a fully automated system, sodium molybdate, which reacts with peroxides in a similar way, replaced the titanium (IV) oxalate which is unstable especially at high temperatures.

In 1959 Saltzman and Gilbert<sup>[68]</sup> have been developed the basic technique of kinetic Colorimetry for the determination of microgram quantities of peroxides by distinguished between hydrogen peroxide and peracetic acid using neutral potassium iodide reagent,

This technique applicable to resolve mixtures of peroxides obtained from atmospheric samples<sup>[68, 81, 82]</sup>.

In 1983 Frew et al<sup>[65]</sup> have been studied the development of quantitative Spectrophotometric method for the determination of peroxides in the concentration range as low as 1 - 10 $\mu$ M ( $10^{-6}$  –  $10^{-5}$  mol dm<sup>-3</sup>) this method based on four assays, (1) based on formation of phenolphthalein or triiodide, (2) iodide oxidation catalytic dye bleaching, (3) coupled oxidation of NADPH, (4) Horseradish peroxidase-coupled oxidations. The four methods in which the reactions with hydrogen peroxide and peracetic acid has been compared the only for the coupled oxidation of NADPH assay significant colour development was found when using metachloroperbenzoic acid (MCPBA) but the other three showed no selectivity for hydrogen peroxide at all.

Davies and Deary<sup>[67]</sup> in 1988 have been determination of peracetic acid in the presence of up to a 1000-fold excess of hydrogen peroxide by using Spectrophotometric method.

This method is similar to the titrimetric method of Sully and Williams, therefore, involves extrapolation of the absorbance change caused by the initial rate of the reaction between hydrogen peroxide and iodide, back to zero time to give a value that similar to the iodine formed due to reaction of the peracid and iodide, this method has been used in the study of the formation of peracetic acid during the perhydrolysis of PNPA.

Flow injection analysis is another method to achieve a continuous observation of the peracetic acid level.

Krussmann and Bohnen<sup>[63]</sup> has been used the peracetic acid to oxidation of iodide to the coloured triiodide ion to detect the peracid. As hydrogen peroxide would lead to false positive results, it is decomposed by the catalase before to the reaction with iodide, therefore requiring an additional reaction step.

Harms and Karst<sup>[83]</sup>, have been development of a very simple flow injection analysis(FIA) methods to determination of peracetic acid this method based on a selective reaction between the peracid and the reagent. The selective oxidation of used for this method is 2, 20-Azino-bis (3-ethylbenzothiazoline)-6- sulphate) (ABTS) with peracetic acid under formation of a green coloured radical cation (ABTS<sup>•+</sup>). Major advantages of this method are the simple experimental setup and the high selectivity towards hydrogen peroxide in the presence of iodide as catalyst at room temperature.

In 1984 Di Furia et al<sup>[84]</sup> found that the Ce(IV) methods fails to give accurate results to determined very small amounts of peracetic acid in solution in the presence of large excess of hydrogen peroxide ,and he was developed anew method which is used a gas – liquid chromatographic method for the determination of peracetic acid in the presence of large excess of hydrogen peroxide and the procedure for this method based on the fact that, the oxidation of an organic sulphide to the corresponding Sulfoxides is very slowly with hydrogen peroxide but very fast with peracetic acid. on this basis, a known excess of sulphide is added to the solution from peracid and hydrogen peroxide the reduction of the peracid within a few seconds whereas hydrogen peroxide is not consumed then by gas- liquid chromatographic measurement the concentration of the peracid from the remaining sulphide concentration and the amount of Sulfoxides formed, simultaneously measured by gas – liquid chromatographic. This method has been applied to determination of 0.002M peracid concentrations (m-chloroperbenzoic acid) in the presence of up to one hundred – fold excess of hydrogen peroxide.

Pinkernell et al has been developed a chromatographic method to determination of peracetic acid and hydrogen peroxide (simultaneous determination) and this method based on the selective oxidation by two reactions step. The first step by using peracetic acid to oxidation of Methyl-p-tolylsulfide (MTS) to the corresponding sulfoxide (MTSO).

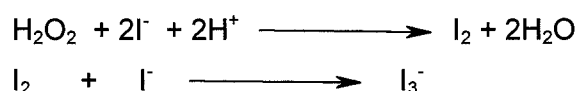
In second step by using hydrogen peroxide to oxidize triphenyl phosphine (TPP) to the corresponding phosphine (TPPO) then can be easily separated all these four compounds by liquid chromatography (LC) with UV detection. The reagents are used as the base for the development of a direct simultaneous method for the LC determination of peracetic acid and hydrogen peroxide in alkaline media. This method required to derivatization of peracetic acid by MTS a pH range between 2 and 6 is required but for hydrogen peroxide the pH required range between 2 and 10.5. So the alkaline samples have to be buffered prior to analysis for using this method therefore there are many disadvantages such as equilibria involving peracetic acid and hydrogen peroxide maybe influenced<sup>[85]</sup> and changes in sample composition may occur based on pH change.

Effkemann in 1998<sup>[86]</sup> by using liquid chromatographic was developed the MPSO/TPP method as the ideal method for the simultaneous determination of hydrogen peroxide and peracetic acid in alkaline media without pH change prior to analysis.

Direct determination of peracetic acid, hydrogen peroxide and acetic acid in disinfectant solutions of peracetic acid and is very simple and rapid in the spectral measurements and analysis by Far-ultraviolet absorption spectroscopy<sup>[87]</sup>, the principle of this method is not required any reagents or catalysts, a calibration standard or any other complicated procedure for analysis. The only required preparation a dilution of hydrogen peroxide with pure water at concentration range lower than 0.2 wt % in sample solutions this method could achieve the detection limit (0.002, 0.003 and 0.01 wt%) peracetic acid , hydrogen peroxide and acetic acid respectively and the response time for the simultaneous determination of the three species in 30s



Also there are another technique recently used to determination of hydrogen peroxide and peracetic acid by using coupled charge device (CCD) Technologies<sup>[88]</sup> This method based on the separation of peracetic acid and hydrogen peroxide on a reverse phase HPLC system followed by post-column reaction with a concentrated solution of potassium iodide as the reaction below with ammonium molybdate as catalyst.



The higher molar absorptivity of  $\text{I}_3^-$  ( $26500 \text{ M}^{-1}.\text{cm}^{-1}$ ) and the detection limit at 352nm HPLC conditions was  $10^{-6} \text{ M}$  levels.

Determination of peracetic acid by flow injection analysis<sup>[89]</sup> [FIA] this method based on a selective reaction between the peracid and the reagent, and suitable for analysis of large numbers of samples in short period of time and for on-line determination of peracetic acid samples especially in industrial processes.

Not all previous techniques have high selectivity and low detection limits, such as Titration methods it is not applied to use when measuring very small amounts of peracetic acid in solution contains a large excess of hydrogen peroxide if used can give some errors, but applied to use at relatively high concentrations.

Photometric, Spectrophotometric and conductivity measurements methods is required a calibration by using peracetic acid as standard solution we known when diluted aqueous solutions of peracetic acid are unstable, another problem is the considerable reactivity toward hydrogen peroxide, also these methods lack for selectivity.

Chromatographic methods have a low detection limit, negligible reactivity toward hydrogen peroxide and can be analyze peracetic acid in the presence of a large excess of hydrogen peroxide in both acidic and alkaline<sup>[71]</sup> media, the problem is time-consuming because of the need for an extraction step with chloroform a solution suitable for gas chromatography.

The main method of peracetic acid measurement employed throughout the course of this research has been based on the titration method in chapter two the formation of peracetic acid and total peroxide content is determined by iodimetric titration, where the peracetic acid reacts with iodine ion faster than hydrogen peroxide. The reaction is carried out in the presence of starch. The initial release of  $I_2$  is measured by thio titration then ammonium molybdate catalyst is added and the  $I_2$  released is further titrated with thiosulphate.

## 1.2 Dyes

Decomposition and hydrolysis of peracetic acid are undesirable since they lead to the formation of products which have no bleaching action; the bleaching action of peracetic acid is mainly the result of epoxidation of the double bonds present in unwanted coloured compounds<sup>[64, 90]</sup>. In chapter three we consider the oxidation of a range of azo, disazo, triarylmethane, quinoline xanthene, indigoid and anthraquinone dyes by hydrogen peroxide or peracetic acid in the presence of different transition metals, and examine the structural features that hinder or contribute to their destruction. The metals used are: Fe(III), Cu(II), Mn(III) and Ag(I). The selection of metal was based on the fact that the transition metals, particularly those possessing two or more valence states between which there is a suitable oxidation-reduction potential, can react with peracetic acid. The metals are also easily obtainable, inexpensive, and relatively low in toxicity. The use of peracids as oxidative systems for dyes, with or without metals, has thus far attracted little interest despite the use of peracid as low temperature oxidants in detergency and other applications for the last two decades. Therefore in this chapter I will be introduction of dyes

Dyes are a kind of organic compound with complex aromatic molecular structures, and like all chemicals, they are similar in their reactions to some other chemicals, and distinctly different from others.

Dyes pollutants disposed to surface water from industrial wastewater. Dye manufacturing plants, textile plants, printing and paper mills discharge their effluent containing dyes into the aqueous environment. Many of these dyes are toxic and

carcinogenic to human. The textile industry plays a major role in the economy in many countries. A very small amount of dye in the water is highly visible and can be toxic to the life in the water, in the textile industry, large quantities of aqueous wastes and dye effluents are discharged from the dyeing process with strong persistent color and high biological oxygen demand (BOD). Due to complex nature of the dyes, wastewaters become bio-resistant. About 1–20% of the total world production of dyes is lost during the dyeing process<sup>[91]</sup>, and is released in the textile effluents. The release of those colored waste waters in the environment is a considerable can originate dangerous by products through oxidation, hydrolysis, or other techniques taking place in the wastewater phase.

### 1.2.1 Colour in dyes

Dyes are characterised in accordance with their capacity to absorb the energy of a particular part of the electromagnetic radiation to which the human eye is sensitive<sup>[92]</sup>. Thus, the colour of the dye is caused by absorbance of electromagnetic radiation. Dyes are aromatic compounds, and the structure fundamentally based on the structure of benzene, as we know, benzene appears to be colourless fluid, In fact it absorbs electromagnetic radiation just as dyes do, but it does so at about 200nm so that we do not see it, at wavelengths between about  $\approx 350 - 750\text{nm}$  when an object absorbs some of the radiation from within that range we see the waves that are left over, and the object appears coloured, the wavelengths just outside the visible range are considered colourless, the colour in dyes to presence of a Chromophore which

delocalised electron systems with conjugated double bond, these are responsible for the absorption of electromagnetic radiation of varying wavelengths, chromophores do not make dyes coloured in the sense that confer on them the ability to absorb radiation rather, chromophores function by altering the energy in the delocalised electron cloud of the dye chromophores,  $-\text{C}=\text{C}-$ ,  $-\text{C}=\text{O}$ ,  $-\text{C}=\text{O}$ ,  $-\text{C}=\text{S}$ ,  $-\text{N}=\text{N}-$ ,  $-\text{N}=\text{O}$ ,  $-\text{NO}_2$ ,  $-\text{C}=\text{NH}$ .

Auxochromes are groups which attach to non ionising compounds yet retain their ability to ionise. The word auxochrome comes from auxo which means increased and chrome means colour, so the word is colour increaser, thus, auxochromes, electron- with drawing or electron donating substituents that cause or intensify the

colour of the chromophore by altering the overall energy of the electron system as summarize the groups which are essential for production of colour is called chromophores and another groups improved the colour called auxochromes , auxochroms such as  $-OH$ ,  $-NR_2$ ,  $-NHR$ ,  $-NH_2$ ,  $-COOH$  and  $-SO_3H$  groups<sup>[93]</sup>. The table (1.4) shows the colour absorbance spectrums.

There are many ways in which colourants cause problems in water

- Concentration of dyes and depending on exposure time.
- Visibility of dyes in water depending on their colour, extinction coefficient and on the clarity of the water
- Dyes absorption and reflection of sunlight entering the water led to the greatest environment concern.

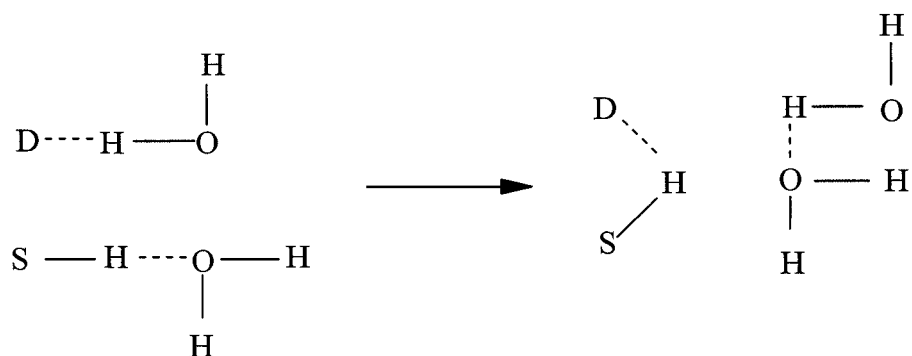
**Table1.4 :- colour absorbance spectrum (Adapted from <sup>[94]</sup>, p254).**

<b>Wavelength of Light absorbed nm</b>	<b>Absorbed light</b>	<b>Visible colour</b>
400 – 435	Violet	<i>Yellowish Green</i>
435 – 480	Blue	<i>Yellow</i>
480 – 490	Greenish Blue	<i>Orange</i>
490 – 500	Bluish Green	<i>Red</i>
500 – 560	Green	<i>Purple</i>
560 – 580	Yellowish Green	<i>Violet</i>
580 – 595	Yellow	<i>Blue</i>
595 – 605	Orange	<i>Greenish Blue</i>
605 - 750	<i>Red</i>	<i>Bluish Green</i>

## 1.2.2 Hydrogen bonds and dyes

Hydrogen bonding occurs when an atom of hydrogen is attracted by rather strong forces to two atoms instead of only one. Typically hydrogen bonding occurs where the partially positively charged hydrogen atom lies between partially negatively charged oxygen and nitrogen atoms, also between fluorine atom in  $\text{HF}_2^-$  and between water and halide ions for example,  $\text{HO-H}\cdots\text{Br}^-$ . This is much quoted in discussions of dye

Binding by substrates when a covalently bound hydrogen atom exists between two electronegative atoms, a hydrogen bond maybe formed. Since appropriate group, e.g.  $\bullet\text{OH}$ ,  $\text{NHR}$ ,  $\text{CF}_3$  etc., are fairly common in dye molecules and substrates it is not surprising that hydrogen bonding should be postulated as a potential binding force for dyes in aggregates and with substrates. The strength of a hydrogen bond depends upon the electronegativity of the bond atoms, therefore  $\text{RNH}_3^+$  contains a more powerful hydrogen bonding atom than  $\text{RNH}_2$ . Hydrogen bond formed between dye molecule and substrate in aqueous medium then the hydrogen bonding require breaking the water hydrogen bonds also hydrogen bonding group in the substrate with the dye molecule will again require hydrogen bonds to be broken, this is aqueous system, hydrogen bonding between dye and substrate will require two hydrogen bonds to be broken for each one formed then will be after two broken hydrogen bonds two water molecules freed to bond together see Scheme [1: 7] below<sup>[95]</sup>.



**Scheme [1: 7]**

### 1.2.3 The molecular excitation model of dye and Aggregation of dye in solution

The change in the absorption spectra of many dyes with changes in concentration, temperature and ionic strength of their aqueous solutions has long been attributed to the tendency of dyes to form dimers or higher aggregates in solution there are a large difference between the absorption spectra of dye aggregates when compared with individual molecules<sup>[96]</sup> this is due to exciton coupling between the transition dipole moment of the individual characteristics molecules<sup>[97]</sup>.

The molecular exciton model qualitatively explains the spectral properties of dye aggregates the individual characteristics in the aggregates of dyes should preserved by chromophores the transition moment of the electronic transition is assumed to be

Localized in the center of the chromophore and its polarization axis parallel to the long axis of the chromophore.

There are many forces between ions and molecules in aqueous solutions Electrostatic interactions between a oppositely charged species and repulsion between the same ions, interaction between “pi” electron systems of adjacent molecules hydrogen bonding also repulsive forces at short distances

### 1.2.4 Classifications of dye

There are two classification of dye<sup>[92, 94]</sup>

- chemical structure (chemical classification) is used by the practising dye chemists who use terms such as azo-dye , anthraquinone dyes or phthalocyanine dyes
- classification by usage or application (colouristic classification) are used by technologist such as reactive dyes for cotton and disperse dyes for polyester, dyes classified according to this method may be anionic, direct or disperse depending on their terminal application.

### 1.2.4.1 Colour index classification

The society of dye and colourists and the American association of textile chemists and colorists have been classified the dyes since 1924 and revised every three months this classification according to the terms of dye colour, structure and application method, Thus all dye are assigned in colour index classification number and each different dye is given a C.I generic name determined by colour and application characteristics also many of dyes and pigments in colour index are placed in one of the 25 structural classes according to their chemical type<sup>[98]</sup>.

Azo dyes (monoazo, disazo, triazo, polyazo) Monoazo dyes have only one N=N double bond, while diazo and triazo dyes contain two and three N=N double bonds, Azo dyes are subdivided into four sections due to the largest class azo dye contain one and three azo linkages , phenyl, naphthyl rings this linkages substituted with functional groups including chloro, hydroxyl, methyl nitro and sulphonate<sup>[99]</sup>.

Anthraquinon dye these dyes constitute the second largest dyes in colour index.

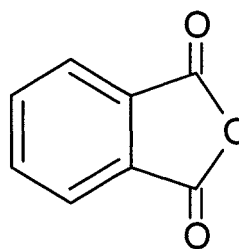
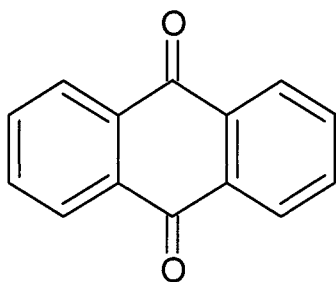
Also phthalocyanine and triarylmethane dyes are quantitatively the most important groups, other groups such as diarylmethane, indigoid, azine, oxazine, thiazine , xanthenes, nitro, nitroso, aminoketone and hydroxy ketone dyes, *Figures (1.2)* shows the most important groups of dyes.

All of these structures allow "π". "π"\* transitions in UV- visible(UV-Vis) area, with high extinction coefficients that allow us to consider these structures.

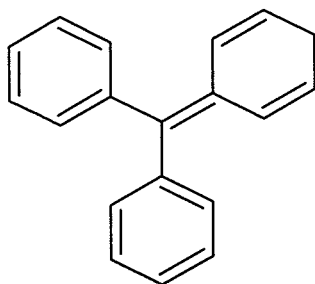


The general structure of the azo dye molecule

(Where R can be an aryl, heteroaryl or  $-CH=C(OH)-$  alkyl derivative)

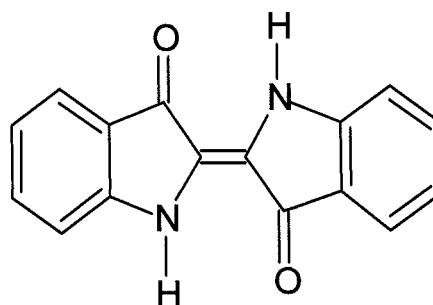


The general structures of Anthraquinone



The general structures of Triarylmethane

the general structures of Phthalocyanine



the general structures of Indigo

Figure 1.2 shows the general structure formulas of several different dyes.

#### 1.2.4.1.1 Acid dyes

Most acid dyes are azo (yellow to red) and the largest class of dyes in the colour Index. Acid dyes are anionic compounds. That is applied to fibers such as silk, wool. The word "acid" refers to the pH in acid dye dyebaths rather than to the presence of acid group carboxyl, sulphonate or amino in the molecular structure making them soluble in water. The chemistry of acid dyes is quite complex dyes are normally very large aromatic molecules consisting of many linked rings. Acid dyes having structures related to triphenylmethane predominate in the milling class of dyes, and many acid dyes are synthesised from chemical intermediates which form anthraquinone like structures as their final state.

#### 1.2.4.1.2 Reactive dyes

In the colour Index classification, the reactive dyes form the second largest dye class with respect to the amount of active entries, the reactive group in dye reactive is often a heterocyclic aromatic ring substituted with chloride or fluoride and this reactive groups in dyes that form double bonds with  $-OH$ ,  $-NH$ , or  $-SH$  groups in fibres. Reactive dyes first appeared commercially in 1956, after their invention in 1954 by Ratte and Stephens. In reactive dye a chromophore contains a substituent that is activated and allowed to directly react to the surface of the substrate. Reactive dyeing is now the most important method for the coloration of cellulosic



fibres. and are the most common dyes used in the textile industry due to their bright colours, good colourfastness and ease of application<sup>[100, 101]</sup>. Reactive dyes are the principal dyes used in the cotton industry which makes up 50% of the world's fiber consumption<sup>[102]</sup>. most of reactive dyes are azo dye Shore in 1990<sup>[103]</sup> Reported that the reactive dye structures are 95 percent azo dyes. or metal complex azo compounds that are linked by an azo group<sup>[104]</sup>. But also anthraquinone and phthalocyanine reactive dyes applied a number of reactive dyes are toxic to many organisms and can cause direct destruction of aquatic life due to the presence of aromatic and metal chlorides<sup>[105]</sup>.

#### **1.2.4.1.3 Direct dyes**

In color Index, the direct dyes forms the second largest dye class with refer to the amount of different dyes: approximately 1600 direct dyes are listed. Many of direct dyes are azo dyes with more than one azo bond or phthalocyanine, oxazine compounds; direct dyes are used on cotton, paper. They are also used as pH indicators and as biological stains. Direct dyes are usually negatively charged, in other words the coloured part of the molecule is the anion. direct dyes are normally carried out in a neutral or slightly alkaline dyebath at or near boiling point with addition of either sodium chloride or sodium sulphate.

#### **1.2.4.1.4 Basic dyes**

In colour index, basic dyes represent about 5% of all dyes listed in the colour index. Basic dyes are water-soluble cationic dye compounds that are used for dyeing acid-group containing fibres. Basic dyes are also used in the coloration of paper. Example for basic dye, diarylmethane, triarylmethanes anthraquinone or azo compounds. Basic dyes have amino groups, or alkylamino groups, as their auxochromes and consequently have an overall positive charge.

#### **1.2.4.1.5 Disperse dye**

In colour Index classification, disperse dyes form the third largest group of dyes, approximately 1400 different compounds are listed, disperse dye are usually small azo or nitro compounds, anthraquinones or metal complex azo compounds,

disperse dyes were originally developed for the dyeing of cellulose acetate, and are substantially water insoluble.

#### **1.2.4.1.6 Metal complex dyes**

In colour index, metal complex dyes are usually azo compounds as aspirate category. Metal complex dyes are strong complexes of one metal atom like copper, cobalt, nickel or chromium and one or two dye molecules.

#### **1.2.4.1.7 Mordant dyes**

The use of mordant dyes is slowly decreasing about 23% of the ~600 different mordant dyes listed in the colour index are in current production. Many mordant dyes are azo, oxazine or triarylmethane compounds, the mordant; potassium dichromate is applied as an after treatment. It is important to refer that many mordant's, especially those in the heavy metal category, can be hazardous to health and more care must be taken when used.

#### **1.2.4.1.8 Pigment dyes**

Approximately 25% of commercial dye names listed in the colour index are pigment dyes, pigment dyes are insoluble, non-ionic compounds or insoluble salts this is due to their crystalline or particulate structure because of their application. The majority of pigment dyes are azo compounds or metal complex and anthraquinone.

#### **1.2.4.1.9 Vat dyes**

Most of vat dyes are anthraquinones or indigoids vat respect to the vats that were used for the reduction of indigo plants through fermentation. Vat dyes are water insoluble dyes. Most vat dyes are less suitable than fiber reactive dyes; indigo is an example of this dye class, vat dyes are widely used for dyeing cellulose fibres.

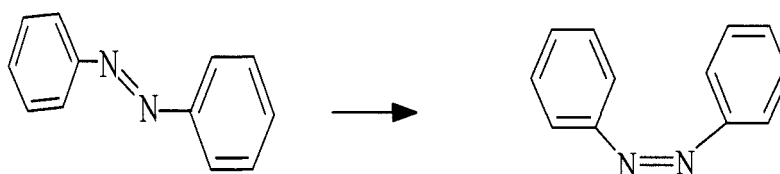
#### 1.2.4.1.10 Solvent dyes

Most of solvent dyes are diazo compounds and non-ionic dyes that are used for dyeing substrates. They are frequently called *lysochrome* dyes. The prefix *lyso* means dissolve, and *chrome* means colour. Solvent dyes are soluble in organic solvents but insoluble in water.

### 1.2.5 Isomerism in azo dye

#### 1.2.5.1 Geometrical isomerisms

Isomerisms are dyes compounds with the same molecular formula but different structural formula



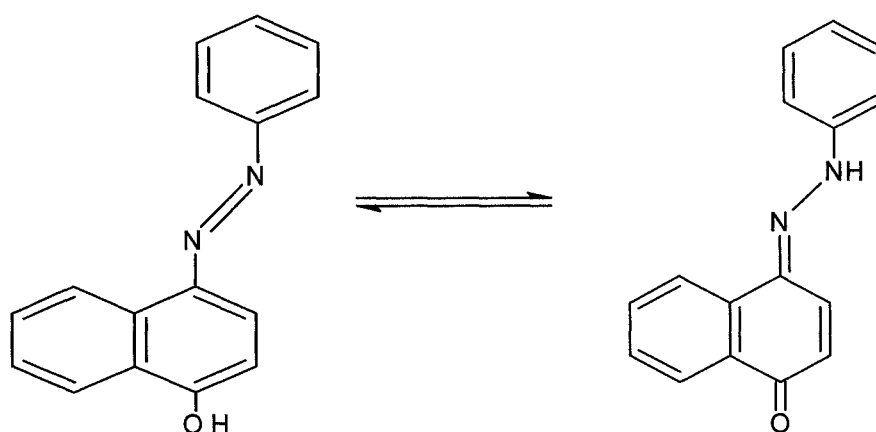
Scheme [1: 8]

#### 1.2.5.2 Tautomerism

Tautomerism are structural isomers of the same chemical substance that spontaneously interconvert with each other and have different chemical properties.

The product obtained from the condensation reaction of phenyl hydrazine with 1, 4-naphthoquinone is the same product obtained from the coupling reaction of benzene diazonium chloride with naphthol<sup>[106]</sup>, the two products gave the azo form in coupling reaction and hydrazone form in condensation reaction. The dynamic equilibrium between the two forms followed of azo-hydrozone tautomerism.

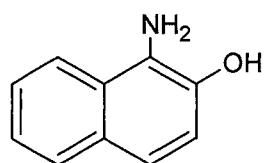
In many organic compounds, there is a mixture of two or more structurally distinct compounds to form rapid equilibrium this phenomenon called tautomerism that it is a Proton shifts from one atom of a molecule to a another molecule<sup>[107]</sup>. In the field of dyes, it is azo-hydrozone tautomerism such as the Scheme [1: 9]



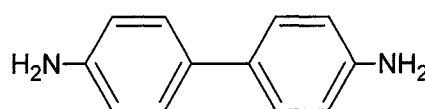
**Scheme [1: 9]**

### 1.2.6 Toxicity of dyes

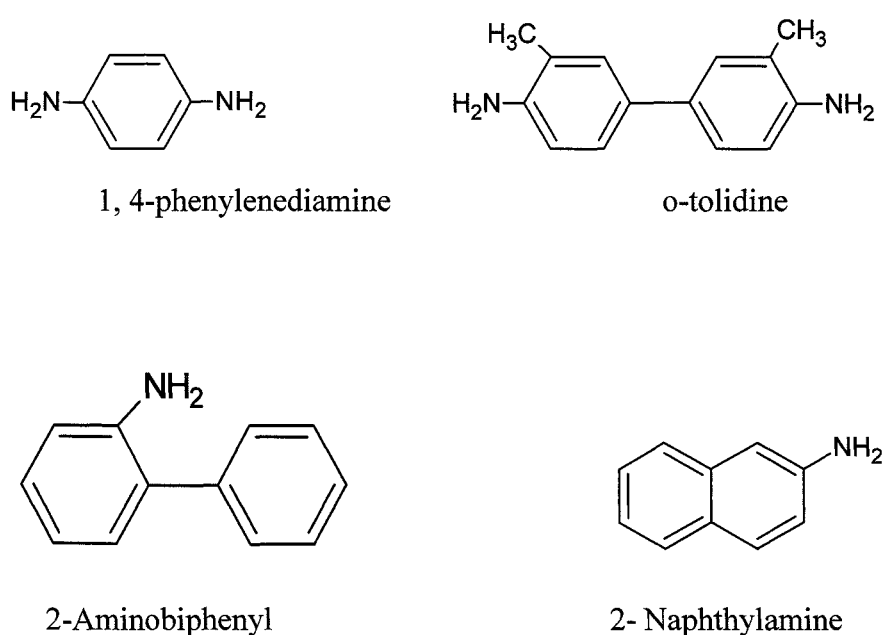
In 1895 Rehn<sup>[108]</sup> showed that increased rates in bladder cancer in workers involved in dye manufacturing. After that time a lot of researches started showing the toxic potential of dyes these toxicity such as mortality, genotoxicity, mutagenicity and carcinogenicity and the most of these researches focused the effects of food colorants, usually azo compounds and dye manufacturing, azo dyes are primarily composed of aromatic amines, substituted benzene and naphthalene rings are common presence of azo dyes. Chung and Cerniglia in 1992<sup>[109]</sup> Reported that all the azo dyes containing a nitro group were found to be mutagenic, further, many of azo dyes when degradation can produce toxic products, for examples 1,4-phenylenediamine, 1-amino-2-naphthol, 2-Aminobiphenyl, 2-Naphthylamine, Benzedrine (prohibited) and substituted benzidines, such as o-tolidine. shows Figure 1.3<sup>[110]</sup>



1-amino-2-naphthol



Benzedrine



**Figure1. 3 Chemical structures show toxic after metabolic activation of azo dyes.**

So azo dyes in purified form are Mutagenic or carcinogenic, only these dyes with free amino group consequently, reduction of azo dyes leads to formation of aromatic amines and several aromatic amines are known mutagens and carcinogens. The toxicity of aromatic amines depends on the structure of the molecule which means the location of the international agency for research on cancer(IARC) suspected most of them amino-sustituted azo dyes fat-soluble azo dyes and benzidine azo dyes some sulphonated azo dyes , many of these dye suspected from (IARC) list were taken out of production, also due to presence of heavy metals and salts in some dye at textile effluents this make complexed in the azo dyes these compounds can cause high electrolyte and conductivity concentrations in the dye wastewater, leading to toxicity problems.

the toxicity of dyes depends on the nature and location of the substituent's which means increase the toxicity with substitution nitro, methyl or methoxy groups or halogen atoms but lower toxicity with carboxyl or sulphonate groups

### **1.2.7 Decolouration**

About 70% of the Earth's surface is covered by water and there is great concern about contamination of these valuable resources. In Europe for example, the new Water Framework Directive seeks to achieve sustainable management of all water resources, ensuring that they meet a minimum quality status by a target date of 2015. Globally it is estimated that only 27% of the existing groundwater, lakes, rivers, polar ice and glaciers-can are adequately protected<sup>[111]</sup>. One of the most pollutants of water is dye, Dyes are considered to be particularly dangerous organic compounds for the environment; about 20% are left in the effluent during the dyeing process. some of them make serious health problems to human the major pollutants comes from textile industry and dye stuff manufacturing industry these pollutants are high suspended solids, chemical oxygen demand, heat, colour, acidity, and other soluble substance , as well as strong colour. The most dyes used in the textile industry are reactive dyes this due to bright colours, ease of application. The removal of dyes from industrial effluents is an area of research receiving increasing attention as government legislation on the release of contaminated.

#### **1.2.7.1 Methods of decolouration of dyes**

There are several factors that determine the technical and economic feasibility of each single dye removal technique these include composition of the waste water, dye type and cost of required chemicals each dye removal technique have its limitations and use of one individual method may not be sufficient to achieve complete decolourisation. The most important removal of hazardous dyes from textile effluent to support the economic and environmental sustainability of the industry<sup>[112]</sup>.the biological methods are cheap and simple to used, but can not be used to many wastewater because most commercial dyes are toxic to the organisms used in the process<sup>[113]</sup>. Traditional methods for treating textile dye waste waters such as coagulation and precipitation<sup>[114]</sup>, adsorption processes<sup>[115]</sup> with activated carbon, however, these processes may be costly, inefficient and often produce a high amount of secondary wastes , more advanced treatment process include electro coagulation technique<sup>[116]</sup> is considered to be potentially an effective tool for treatment of textile waste waters, Ultrasonic decomposition<sup>[117]</sup>, Uv

or combined oxidation processes<sup>[118]</sup>. The combined photochemical and biological processes<sup>[119]</sup>. Ozonation<sup>[120-123]</sup>, advanced chemical oxidation<sup>[124]</sup>, electrochemical oxidation<sup>[125, 126]</sup>, Fenton's reagent<sup>[127]</sup>, ozone and Fenton's reagent<sup>[128]</sup>, supported liquid membrane<sup>[129-131]</sup>, generally, the time needed for decoloration to occur varies from dye to dye which means impossible to make a general rule each method has advantages and disadvantages the most important methods is

## **1.2.7.2 Chemical decolouration methods**

### ***1.2.7.2.1 Oxidation Techniques***

Chemical oxidation is the most widely used techniques for the decolorization process in research and applied in industry, because that is due to diversity of chemical processes that can be effective these techniques include oxidation reactions, photochemical oxidations and electrochemical treatment. electrochemical technology has been applied to effectively remove acids as well as dispersed and metal complex dyes, Naumczyk, et al <sup>[132]</sup>, have been described the electrochemical techniques for the treatment of dye waste are more efficient than other treatments.

Chemical oxidation can be applied for one of several purposes in a wastewater treatment process depending on the results desired. These are

- treatment of toxic organics at low concentrations in groundwater,
- treatment of low volume-high strength waste-waters and enhanced biodegradability,
- treatment of waste-waters and normally subject to bio-oxidation e.g., cyanide and complex metals,
- Detoxification relative to aquatic toxicity following of biological treatment. Normally, some of biological treatment will be the most-effective technology for organic wastewater. Some organics, however, are either non-biodegradable or are toxic either to the biological process or to aquatic life and must therefore be pre or post treated.

The chemical oxidation is a very attractive technique for the purification of water contaminated with organic substances, especially with those, which are too toxic for

biological degradation. However, the direct reaction of organic molecules with oxygen, carried out at ambient temperatures, is usually too slow to be of practical use. Oxidation can be accelerated using high temperature as well as electric energy, but the application of these methods is not very extensive.

As environmental needs and regulations continue to become more severe through the 2000's, destructive treatment technologies consistent with waste minimization must be developed. Oxidation technologies are capable of achieving desired on site pollutant destruction and of hazardous wastes present a commercially viable alternative to meet these increasingly demanding needs. If carried out to its ultimate stage, oxidation can completely oxidize organic compounds to carbon dioxide, water and salts. Partial oxidation can result in increased biodegradability of pollutants so that; residual organic compounds can be removed through biological treatment. Many biological processes are, in fact, oxidative processes. or by bleaching, bleaching one of the best method for decolouration.

#### **1.2.7.2.2 Bleaching**

Bleaching has been defined as the structural modification of a coloured substance to give a colourless or less intensely coloured product. The process of bleaching can take place either in solution, or on the cloth. Bleaching agents range from oxygen, ozone, peroxides, chlorine and oxides of chlorine on one hand to sulphur dioxide and bisulphite ions on the other. The first method of bleaching used by Romans which was used sulphur dioxide fumes to bleach woollen goods and this method still used until the emergence of cheap hydrogen peroxide , bleaching by bisulphite( $\text{HSO}_3^-$ ) is the active species<sup>[133, 134]</sup>, there are disadvantages from using sulphur dioxide bleaching such that the substrate is reduced during bleaching and can be slowly oxidised back to its coloured form by aerobic oxygen. The numerous change in the textile industry after prepared bleaching powder (calcium hypochlorite) in eighteenth century because this bleaching powder is easy to use and store the solution very good bleaching medium for cellulosic fibres, then calcium hypochlorite replaced by sodium hypochlorite because there were no difficulties caused by the insolubility of residual unreacted hydroxide there are also disadvantages from using hypochlorite such as formation of highly toxic chlorinated organic by-products during the bleaching process, hydrogen peroxide is a weaker



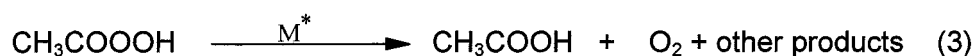
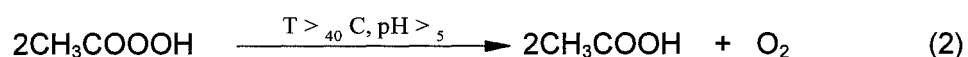
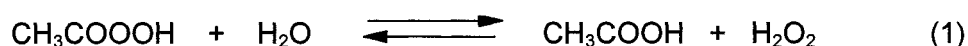
oxidising agent than hypochlorite and can be used to bleach polypeptide as well as cellulose fibres with much less risk of fibre damage.

Sodium perborate ( $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ ) and percarbonate ( $2\text{NaCO}_3 \cdot 3\text{H}_2\text{O}_2$ ) these two compounds used to produce hydrogen peroxide when dissolved in water, thus, can be used in domestic washing powders but require the high pH and high temperature to be effective.

An environmentally safe alternative to hypochlorite is peracetic acid at last few years, hypochlorite is being replaced by peracetic acid<sup>[135]</sup>, because PAA when it decomposes give oxygen and acetic acid this processes completely biodegradable, furthermore peracetic acid is higher brightness values with less fiber damage<sup>[135]</sup>, as well as better than hydrogen peroxide because that the a satisfactory degree of whiteness can be obtained at  $60^\circ\text{C}$  in 40 minutes at neutral pH without the addition of auxiliary agents, at lower energy and water consumption when rinsing of the fabric,

there is also much less damage to the cotton fibre when peracetic acid is used<sup>[136-139]</sup>. the bleaching action of peracetic acid is mainly the result of epoxidation of the double

bonds present in unwanted coloured compounds the equations in Scheme [1:10] shows the mechanism of peracetic acid, hydrolysis, decomposition and oxidation<sup>[140]</sup>.



**Scheme [1: 10]**

#### 1.2.7.2.2.1 Mechanisms of bleaching

1. **Reductive Bleaching:** - such that action of sulphite on aromatic nitro compounds or bisulphite on carbonyl compounds could cause a decrease in

the length of the conjugated system accompanied by a shift towards the ultraviolet part of the spectrum. the reaction can often be reversed by aerobic oxidation of the bleached material

2. **Oxidative bleaching:** - generally involves disruption of the conjugated system of the coloured molecule-often going as far as the breakdown of the molecule into smaller fragments. The reaction can go via a free radical, electrophilic or nucleophilic attack on the substrate.

The synthetic organic chemicals that are being regulated to lower levels today are those which do not readily lend themselves to simple oxidative treatment. Depending on the nature of the oxidant, potentially hazardous by-products may be formed, e.g., chlorinated intermediates in chlorination processes. To minimize these by-products, uses of oxidants involving oxygen are being investigated. Oxygen itself is generally kinetically too slow to be practical, or requires severe conditions of temperature and/or pressure to effect complete oxidation. Active oxygen products, such as hydrogen peroxide and peracetic acid, are capable of providing the desired oxidation in many cases.

Other techniques are used recently for decolourization which called advanced oxidation process (AOPs). Are currently subject to a rapid evolution, especially those involving catalytic and/or photochemical systems, the successful application of AOPs depends primarily on the nature of the pollutants. Currently, only AOPs are considered to have the capacity for the complete elimination of the contamination. Complete oxidation, i.e. mineralization of organic pollutants. The most important in advanced oxidation process are briefly discussed in sections below.

### 1.2.8 Advanced oxidation process (AOPs)

In 1987, Glaze et al<sup>[141]</sup>, defined advanced oxidation processes as “near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radicals in sufficient quantity to effect water purification”.

Since the early 1970s advanced oxidation processes (AOPs) have been used to remove both low and high concentrations of organic compounds because the

treatment of waste water containing organic compounds like aromatic rings such as dyes , dyestuffs, chlorophenols by methods such as physical- chemical treatment(flocculation, precipitation and absorption) are not effective <sup>[142]</sup> or method such as traditional biotreatment<sup>[143, 144]</sup> in the advanced oxidation processes, the organic compounds can be completely converted to carbon dioxide and water mainly by hydroxyl radical<sup>[145, 146]</sup>. the hydroxyl radical which is the most powerful oxidizing agent generated ,this is due to ( $\bullet\text{OH}$ ) is acts very rapidly with most organic compounds, and this is as a results of oxidation and reduction which means transfer of one or more electrons from an electron donor (reductant) to an electron acceptor (oxidant) during to these processes from electron transfers producing chemical species with an odd number of valence electrons, these species called a radical and because one of their electrons is unpaired these species tend to be highly unstable and , thus ,highly reactive, so there are another oxidation reaction between the radical oxidants and other reactants until to reach stable oxidation products are formed to summarize above the advanced oxidation processes have two routs of oxidation (1) the formation of strong oxidants such as ( $\bullet\text{OH}$ ) (2) The reaction of these oxidants with organic contaminates in water. So the advanced oxidation processes is used to decompose many hazardous chemical compounds to acceptable levels, without producing addition hazardous by products or sludge which required further handling. Table1.5; - shows the relative oxidation power of some oxidizing species

Hydrogen peroxide is currently considered the most appropriate reactant for use in these technologies

**Table 1.5:- Relative oxidation power of some oxidizing species<sup>[147, 148]</sup>**

Oxidizing species	Relative oxidation power
Chlorine	1.00
Hypochlorous acid	1.10
Permanganate	1.24
Hydrogen peroxide	1.31
Ozone	1.52
Atomic oxygen	1.78
Hydroxyl radical	2.05
Positively charged hole on titanium dioxide, $\text{TiO}_2^+$	2.35

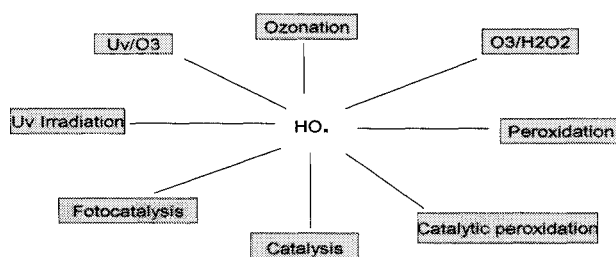
### 1.2.8.1 Methods generating •OH radicals

These involved photochemical and non- photochemical methods

Figure (1.4) shows the most popular techniques used recently for generation •OH to decolourization of dyes<sup>[149]</sup> is:-

Oxidation with Fenton's reagent ( $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$ ) photo catalysis and Ozonation ( $\text{H}_2\text{O}_2$  – Ozone), ( $\text{H}_2\text{O}_2$  – UV) radiation, Ozone / Ultraviolet Light ( $\text{O}_3$  /UV) ,  $\text{H}_2\text{O}_2$  / ozone / ultravioleta ( $\text{H}_2\text{O}_2$  / $\text{O}_3$  /UV), Photocatalytic oxidation (UV/  $\text{TiO}_2$  ) , $\text{H}_2\text{O}_2$  – peroxidise, peroxidise can also be used as hydrogen peroxide activator the efficiency of peroxidise

for the treatment is depends on the peroxidise used, concentration, pH, temperature of the medium. Thus, these techniques have been shown great potential for effectively removing dyes from waste water. These techniques based on the generation of highly reactive radical species, such as hydroxyl radical (•OH) which reacts with dye molecules<sup>[150]</sup> .the hydroxyl radical is a powerful oxidant and starts cascade of oxidation reactions that can in the end lead to total mineralization of organic pollutants .



**Figure 1.4 Advanced oxidation processes<sup>[149]</sup>.**

### 1.2.8.2 H<sub>2</sub>O<sub>2</sub>-UV radiation

Hydrogen peroxide alone is ineffective to oxidization of the textile wastewater under both conditional acid and alkali values<sup>[151]</sup>. But under UV-irradiation H<sub>2</sub>O<sub>2</sub> are photolysied to produce two •OH radicals<sup>[76]</sup>.



thus hydrogen peroxide is activated by UV- light and there are many factors depending on treatment by H<sub>2</sub>O<sub>2</sub>-UV such as H<sub>2</sub>O<sub>2</sub> concentration in the intensity of UV- irradiation, pH, also dye structure . Shen Y.S. and Wang D.K. in 2002 <sup>[152]</sup> have been investigated the relationship between UV-light intensity and decomposition in Uv/H<sub>2</sub>O<sub>2</sub> process and found the decomposition rate of dye increase with increasing UV light intensity.

Shu et al <sup>[153]</sup> in 1995 have been found that acid dyes are that the easiest to decompose and the decolouration effectiveness decreases by increasing number of azo groups.

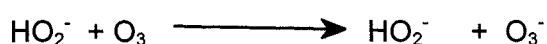
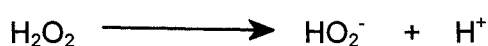
Pittroff <sup>[154]</sup> have been reported that the decolourisation is more rapidly at at reactive dyes and direct, metal-complex and disperse dyes but dyes have colour yellow and green reactive dyes is very slowly which means need longer reaction time.

### 1.2.8.3 Ozone, O<sub>3</sub> / UV

Rein M in 2001<sup>[155]</sup> have been found the Ozonation of organic compounds does not lead to oxidize organic to CO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> and they found the intermediate formation in some solution after oxidation maybe toxic or more toxic than initial compounds whereas the UV radiation could lead to complete the oxidation reaction by supplement the reaction with it . Hung-Yee in 1995 Reported that the ineffective decolorizing of dyes by UV or O<sub>3</sub> alone but the effective method of decolourizing of dye when combination of O<sub>3</sub> with UV (O<sub>3</sub>/UV). the efficient of ozone photolysis at UV radiation 254nm wavelength and can be formation Hydrogen peroxide as an intermediate, this lead to decomposes to •OH<sup>[76]</sup>.

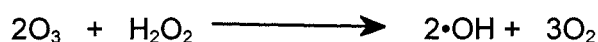
### 1.2.8.4 H<sub>2</sub>O<sub>2</sub> -Ozone (peroxone)

The addition of both H<sub>2</sub>O<sub>2</sub> and ozone to wastewater accelerates the decomposition of ozone and enhances formation of the hydroxyl radical <sup>[76]</sup>.



Stachlin and Hoigne in 1982 <sup>[77]</sup> have been reported that the reaction of H<sub>2</sub>O<sub>2</sub> with O<sub>3</sub> are very slowly at acidic pH, but more rapidly decomposition by H<sub>2</sub>O<sub>2</sub> at pH values above 5 .

The combination of H<sub>2</sub>O<sub>2</sub> with two ozone molecules formation two .OH radicals.



Decolouration by this method is suitable for direct, metal-complex or blue disperse dyes <sup>[156]</sup>. But some problems with decolouration of acid dyes<sup>[156]</sup>.

More effective has been demonstrated when combined H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> process than H<sub>2</sub>O<sub>2</sub>/ or O<sub>3</sub> alone to remove pollutant and other synthetic organics, Therefore when combined H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> to produce hydroxyl radicals more than just O<sub>3</sub> which allows a lower dosage of O<sub>3</sub> to be used. This is desirable for reducing costs.

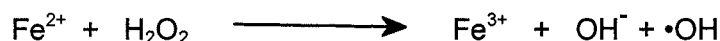
#### 1.2.8.5 Ozone – H<sub>2</sub>O<sub>2</sub> – UV-radiation (O<sub>3</sub>/ H<sub>2</sub>O<sub>2</sub>/Uv)

The efficiency of O<sub>3</sub>/ UV- system for accelerates the decomposition of zone, increased by addition of hydrogen peroxide to combine (O<sub>3</sub>/ H<sub>2</sub>O<sub>2</sub>/UV) the results increased rate of •OH generation<sup>[157]</sup>.

Azbar *et al.*, 2004 <sup>[142]</sup> have been Reported that the most efficient for decolouration of dye house wastewater and polyester fiber dying process and acetate by combination of (H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/UV).

#### 1.2.8.6 Fenton system (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>)

Fenton, <sup>[158]</sup> have been discovered Fenton process from 1884 for maleic acid oxidation:



Fenton's reagent (hydrogen peroxide, activated by Fell salts is very applicable for the oxidation of wastewaters, this due to the rate constant for reaction of ferrous ion with H<sub>2</sub>O<sub>2</sub> is high and Fell oxidizes to FeIII very quickly even at excess amounts of H<sub>2</sub>O<sub>2</sub>.

The Fenton's system has the capacity to completely decolorize and partially mineralize textile industry dyes in short reaction time, as documented by some studies<sup>[137, 139, 159]</sup>.

The main advantages of use (Fe<sup>2+</sup>/ H<sub>2</sub>O<sub>2</sub>) as an oxidant iron is a highly abundant and non-toxic element and the H<sub>2</sub>O<sub>2</sub> is easy to handle and environmentally benign.

Also Fe(III) – oxalate complexes were used as a kind of catalyst in the photodegradation of textile dyes in water<sup>[160-162]</sup>.

#### 1.2.8.7 Photocatalytic oxidation (Uv/TiO<sub>2</sub>)

One of the most widely used metal oxides in industry is Titanium dioxide, both in the forms of anatase and rutile also its use as a catalyst support or as a catalyst

and photocatalyst it self. the  $\text{TiO}_2$  as photocatalyst is one of the most advanced oxidation processes used recent years, the basis of photocatalysis is the photo-excitation of a semiconductor that is solid as a result of the absorption of electromagnetic radiation, as,  $\text{TiO}_2$  is illuminated by light with wave length less than 380nm, the photons excite valence band electrons a cross the band gap in the conduction band, then leaving holes behind in the valence band. After that the holes in  $\text{TiO}_2$  react with water molecules or with hydroxide ions to produce  $\bullet\text{OH}$  radicals, therefore generation of hydroxyl radicals depends on the solution pH.

There are many studies has been investigated the dye by photocatalytic oxidation and amenable to oxidize a wide variety of toxic and organic compounds to harmless e.g carbon dioxide and water <sup>[163]</sup>.

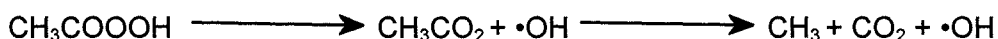
in furthermore titanium dioxide interacts with the supported phase as a promoter <sup>[164]</sup>. This technique are used to the interaction between chloride ions and  $\bullet\text{OH}$  radicals in photocatalytic treatment of reactive dye based on  $\text{TiO}_2$ , the chloride ions could react with  $\bullet\text{OH}$  radicals and reduce the amount of  $\bullet\text{OH}$  radicals a available for the oxidation reaction.

### 1.2.9 Reduction processes.

Reduction processes are also widely used for the decolourization of dyes.

We have seen from all of these processes can produce hydroxyl radicals, which can react with and destroy a wide range of organic contaminants.

Also peracetic acid might be a convenient source of  $\bullet\text{OH}$  hydroxyl radicals both in the gas phase and in solution, the radicals being formed by sequence of reactions <sup>[165]</sup>.



The second order rate constant of oxidation of the organics with hydroxyl radicals range from  $10^8$  to  $10^{11} \text{ M}^{-1} \text{ S}^{-1}$  and the reaction rate constants of molecular ozone with different organic compounds are also given in Table (1.6).



**Table 1.6 Reaction rate constants ( $k$ ,  $M^{-1} s^{-1}$ ) of ozone vs. hydroxyl radical <sup>[166]</sup>**

Compound	O <sub>3</sub>	•OH
Chlorinated alkenes	$10^3-10^4$	$10^9-10^{11}$
Phenols	$10^3$	$10^9-10^{10}$
N-containing organics	$1-10^2$	$10^8-10^{10}$
Aromatics	$1-10^2$	$10^8-10^{10}$
Ketones	1	$10^9-10^{10}$
Alcohols	$10^{-2}-1$	$10^8-10^9$

### 1.2.10 Disadvantages of advanced oxidation Process

There are disadvantages to AOPs under certain circumstances. For example: ozone must be produced on site, and is expensive; the Fenton system, using hydrogen peroxide and ferrous ions produces a lot of ferric sludge, and the pH<sup>[167]</sup> of the system must be strictly controlled by the addition of mineral aids such as sulphuric acid; and UV irradiation is ineffective in soil matrices or strongly absorbing solutions. There is, moreover, a fundamental problem with AOPs in circumstances where biorefractory pollutants are mixed with easily degradable ones, or with natural organic compounds from the breakdown of living organisms. The very strength of AOPs is the production of hydroxyl radicals that are strong and indiscriminate oxidants. In mixed pollutant environments the oxidising power is wasted on chemicals that are harmless or easily degraded by natural processes. A profound weakness of the Fenton (hydrogen peroxide-ferrous) system is that a rapid burst of hydroxyl radical is produced, so that in dilute solutions of pollutants most of the oxidising power of the peroxide is dissipated in wasteful O<sub>2</sub> production via superoxide, HOO formed from the reaction of hydroxyl radicals and hydrogen peroxide.

### **1.2.11 Physical methods of decolouration**

There are several known methods these included traditional physical- chemical techniques (ultrafiltration, reverse osmosis, ion exchange, coagulation- flocculation and adsorption),

#### **1.2.11.1 Ultrafiltration**

Ultrafiltration which means filtration with bigger pores this technique is suitable as pre-treatment<sup>[168]</sup> or in combination with a biological reactor<sup>[169]</sup>, but in generally not successful as the membrane pore size is too large to prevent dye molecules from passing through.

#### **1.2.11.2 Coagulation- flocculation**

coagulation- flocculation treatments are generally used to eliminate organic substances, but the chemicals normally used in this process have no effect on the elimination of soluble dyestuffs, but effectively eliminates insoluble dyes<sup>[170]</sup>

the technique of coagulation-flocculation is based on the addition of a coagulant followed by a generally rapid association between the coagulant and the pollutants, then produce coagulates or flocks subsequently precipitated are then removed by either flotation, by further treated to reduce its water content and toxicity<sup>[171, 172]</sup>

the last few years have been developed organic anionic, cationic or non- ionic coagulant polymers rather than inorganic coagulants( aluminium, magnesium, calcium and iron salts), for colour removal treatments, in addition they offer advantages over inorganics such as lower toxicity and improved colour removal ability and lower sludge production<sup>[173, 174]</sup>

#### **1.2.11.3 Adsorption**

The main abiotic mechanism for removing dyes from the wastewaters is adsorption on sludge quality and this technique is more popular because of great efficiency in the removal of pollutants too stable for conventional methods. Activated carbon is the most used method of dye decolorization by adsorption, to contrast with peat, fly

ash, and coal, wood chips and corncob and is very effective for adsorbing cationic, mordant and acid dyes<sup>[175, 176]</sup>.

The second adsorbent, suitable for wastewater treatment called biomass

Biomass decoloration of azo dye is a result of two mechanisms adsorption into solid matrix and ion exchange which depends on the dye molecule size and charge, pH of medium and salt concentration.

The main disadvantage of adsorption processes needs to be regenerated this led to increase the cost of the process.

### **1.2.12 Biological degradation**

Biological degradation or breakdown by living organisms

The most important removal process of organics biological degradation or breakdown by living organisms which means are transferred from industry processes into solid and aquatic ecosystems, biological degradation are different depending on the presence or absence of oxygen<sup>[177]</sup>, there are a wide range of micro-organisms including bacteria, fungi, and algae are capable of efficiently decolourising a wide range of dyes also used

Anaerobic-aerobic (combined) biodegradation there is a complete decolourisation of dyes and significant reduction in BOD and COD levels. The most important of biological degradation is bacteria and fungi.

#### **1.2.12.1 Bacterial**

There are variety of studied has been investigated that the ability for both bacteria to metabolize and bacteria with specialized reducing enzymes to aerobically degradation of certain azo dyes<sup>[178-180]</sup>, at aerobic conditions azo dyes are not readily metabolized but under anaerobic conditions many bacteria reduce azo dyes by the activity of unspecific, soluble, cytoplasmatic reductase.

The first step in the biodegradation of azo dye reduction resulting in the formation of the aromatic amines<sup>[181]</sup>, and these aromatic amines some times toxic, mutagenic<sup>[182]</sup>, it is necessary to another step to achieve complete degradation of azo dye to avoid toxicity of dyes and this steps involves aerobic biodegradation<sup>[183]</sup>, therefore biological treatment strategy based on anaerobic

reduction of the azo dyes, followed by aerobic transformation of the formed aromatic amines.

In non azo dyes such as aerobic decolourization of triphenylmethane dyes<sup>[184]</sup>, bacterial biodegradation can be degradation of anthraquinone dyes<sup>[185]</sup>, under anaerobic conditions can be degradation of phtalocyanine dyes<sup>[186]</sup>.

#### **1.2.12.2 Fungal**

The use ligninolytic fungi is one of the possible alternatives studied for the biodegradation of dyes, fungi is responsible for the decolorization and degradation of a number of dyes<sup>[182]</sup>. White-rot fungi in particular produced enzymes as lignin peroxidise, manganese peroxidise that degradation of many aromatic compounds due to their non- specific activity<sup>[180]</sup>.

#### **1.2.13 advantages and disadvantages of methods of dyes**

The table 1.7 shows advantage and disadvantages of some methods of dyes removal from wastewater.

**Table 1.7:- The advantages and disadvantages of some methods of dyes removal from wastewater. Adapted from <sup>[187]</sup>.**

Method	Advantages	Disadvantages
Adsorption	low cost no regeneration needed dye-adsorbed materials can be used as substrates in solid state fermentation	some adsorbents have low surface area possible side reactions loss of adsorbents performance depends on wastewater characteristics
Nanofiltration	removes all dye types high effluent quality easy to scale-up	high investment costs membrane fouling effluent must be treated
Electro coagulation	removes small colloidal articles no use of coagulants low sludge production low cost	not effective for all dyes
Coagulation and perception	effective for all dyes	high cost high sludge production
Advanced chemical oxidation	non-hazardous end products	high cost
Electrochemical oxidation	no sludge production breakdown compounds are non-hazardous no chemicals used	high cost
Photo oxidation	no sludge production	releases aromatic amines
Ozonation	no sludge production no alteration of volume	high cost short half life
Supported liquid membrane	minimal loss of extractants simple to operate low energy consumption easy to scale up low cost	emulsification may occurs
Liquid-liquid extraction	low cost low energy consumption variety of solvents available easy to scale-up	emulsification may occur effluent must be treated
Biological processes	environmentally friendly public acceptance economically attractive	slow process needs adequate nutrients narrow operating temperature range

### 1.3 Aims of this project

The research programme aims to compare existing advanced oxidation process (AOPs) with new approaches that either depends on the formation of alternative peroxide species from hydrogen peroxide or which use less extreme conditions of pH than are necessary for the Fenton reaction. The kinetics and equilibria of peracid formation from hydrogen peroxide and parent carboxylic acids will be studied under a range of aqueous conditions with a variety of catalysts. The properties of the resulting equilibrium mixture will be investigated in terms of its reactivity toward model pollutant substrates. For certain reactions it is known that the ferrous ion catalysed reactions with peracetic acid are faster than the corresponding reactions with Fenton's reagent<sup>[188]</sup>. The effects of catalysts, light, and other perturbations on the reactivity of the equilibrium mixture are assessed and compared with their effects on the reactivity of hydrogen peroxide alone under comparable conditions.

Davies and co-workers have carried out a number of studies of peroxide bleach activators, where peracids and acyl peroxides are formed via acyl transfer from an ester or amide activator molecule to hydrogen peroxide<sup>[189]</sup>. Peracids are much more powerful oxidants than hydrogen peroxide but much more specific oxidants than hydroxyl radicals. The use of activator molecules to form peracids vastly reduces the atom efficiency of the process in Green Chemical terms. Alternatively, peracids can be prepared directly from the reaction of hydrogen peroxide and the parent carboxylic acid at low pH. The reaction of acetic acid and hydrogen peroxide in dioxin, for example, has an equilibrium constant  $\frac{[\text{peracetic acid}][\text{H}_2\text{O}]}{[\text{acetic acid}][\text{H}_2\text{O}_2]}$  about 0.8, and is acid catalysed[18]. This extrapolates to an equilibrium constant  $\frac{[\text{peracetic acid}]}{[\text{acetic acid}][\text{H}_2\text{O}_2]}$  of about  $0.015 \text{ M}^{-1}$  in water. ( $[\text{H}_2\text{O}] = 55 \text{ M}$  in water). The equilibrium constant should be independent of pH up to the pKa of acetic acid, 4.7, and thereafter drop with decreasing  $[\text{H}^+]$  until pH 8.2, the pKa of peracetic acid, where it will level out at about  $5 \times 10^{-6} \text{ M}^{-1}$ . When peracids oxidise organic compounds the parent carboxylic acid is often regenerated and so, under appropriate conditions, simple biodegradable carboxylic acids can act as catalysts for the reactions of hydrogen peroxide.

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